UNIVERSITY OF EDINBURGH

An investigation of diffusivity in liquids and its application to mass transfer between gases and liquids.

Narain Prasad Agarwalla, B.Sc. (Calcutta).
Dip. Tech. Chem. (Edin.)

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C O N T E N T S

SUMMARY

Part I. The importance of the study of diffusivity of gases in liquids with special reference to gas absorption is discussed.

Part II. **Section A.** The diffusion coefficient is defined and classified. Theoretical relations leading to experimental determination of diffusivity under different experimental conditions are stated. The equations of Stokes - Einstein, and of Eyring; the law of the particle, and diffusion from a spherical shell and from a hollow cylinder are considered.

Section B. The relation between diffusivity and rate of mass transfer as incorporated in the theories of Lewis - Whitman, of Higbie, and of Danckwerts are discussed and compared.

The "first order process" theory is mentioned.

Implications of the three theories of gas absorption and an approach to them on the basis of experimental data on D and k_L are discussed.

A new diffusion coefficient applicable to relations involving mass transfer is suggested.

Part III. **Section A.** Experimental methods of determining diffusivity in liquids are reviewed.

Section B. Preliminary experiments to decide the apparatus and procedure for determining diffusivity of gases in liquids and for analysing such systems are described.

Part IV. The apparatus and procedure for determining diffusivity are described and the results given. A new technique is adapted in later experiments which is described and the results given.

Part V. Section A. The two methods of determining diffusivity are compared. Variation of diffusivity with concentration, with temperature, and with viscosity of the medium is discussed.

Section B. An attempt is made to define the relationship between D and k_L on the basis of experimental data.

Experimental values of k_L are compared with those predicted by the relations of Higbie and of Danckwerts.

PART I

PART I

Introduction

Mass Transfer

The movement of one or more components within or between phases occurs in many unit operations of chemical engineering and is known as mass transfer. It is caused by the existence of a concentration gradient of a component within a system, the potential available tending to transfer the component in the direction of decreasing concentration. Absorption, crystallisation, extraction, stripping, humidification and drying are all examples of mass transfer operations.

Diffusion and Mass Transfer

In most of the mass transfer operations, there are two main mechanisms of transfer, one by molecular or true diffusion as a result of concentration gradients and the other by actual bulk motion of the fluid (convection). In such operations usually there exists a film of relatively stationary material which insulates the main body of fluid from the other phase and a main body where the fluid is turbulent and eddying. While the two mechanisms operate simultaneously throughout the system, in the true film where turbulence is practically negligible the transfer is mainly by molecular diffusion, while in the main body the transfer is mostly by convection due to the rapid eddying. Thus a

substance being transferred must pass through the two consecutively, being carried by turbulence through the main body of the fluid and then by true diffusion through the film to the interface. Although the interfacial area between the two phases may be increased through violent agitation, the thin films cannot be eliminated entirely and it is generally accepted that in all operations involving two phases such films may exist on either side of the interface with the result that diffusion is a necessary step in the transfer from one phase to another. Such films, if thin, may offer only slight resistance to the process of mass transfer and so have a negligible effect. On the other hand, they may, and they frequently do, exert the greater resistance to the process of mass transfer and so may control the rate of the process.

The overall process, however, may be evaluated on the basis of the knowledge of the quantitative contribution of molecular diffusion and turbulence at various points in the system. Since the extent to which these two mechanisms control the overall process is not precisely known, it is customary to express rates of mass transfer in terms of an overall transfer coefficient. The procedure is purely empirical and there is no logical justification for its use especially if Henry's law is not obeyed. In such cases, it has been found that the rates of transfer may not vary in direct proportion to the overall bulk concentration differences at all concentration levels, although the rates may be proportional to the concentration difference in each phase taken separately. In

view of this fact, it is desirable that both eddy diffusion rate and true diffusion rate should be studied separately, if a more precise knowledge of the mechanism of mass transfer is required.

Eddy Diffusion

While it is possible to describe molecular diffusion in mathematical terms quite satisfactorily at present, an adequate knowledge of the mechanism of eddy diffusion is still lacking. The motion of turbulence cannot be described completely in mathematical terms yet and the derivation of relations similar to those for diffusion, giving the rate of mass transfer by turbulent mechanism has not been possible. A very brief account, however, is given here of the progress made.

One of the earliest mathematical treatment of eddy diffusion was by Wilson[1] who derived a relation between eddy diffusivity E and the volumetric concentration of the diffusing gas C at an axial distance x down stream from a continuous point source in a fluid moving with a uniform velocity u of the form:

$$C = \frac{Q}{4\pi E R^1} e^{-(u/2E)(R^1-x)}$$

where Q is the volumetric feed rate and R^1 is the direct distance from the injector tube to the sampling point.

Later Taylor[2] proposed a theory based on the statistical theory of turbulence in which the variations in the properties defining turbulence were treated statistically. His treatment leads to the equation:

$$E = u' L_e$$

where E is the eddy diffusivity, u' is the root-mean-square deviating velocity and L_e is a characteristic length of the system. This is similar to the relation obtained recently by Dryden[3] based on the mixing-length theory, viz.:

$$E = 0.5\, u' L$$

where u' is the deviating velocity normal to the direction of flow (assuming unidirectional diffusion), and L is the Prandtl mixing-length, i.e., the distance that a particle of fluid, or eddy, travels before losing its identity.

The experimental study of eddy diffusion has not been considerable, the work of Schubauer[4]; of Towle and Sherwood[5]; of Sherwood and Woertz[6]; and of van Driest[7] being most noteworthy. Although their results do not justify the validity of the above relations completely or give a satisfactory picture of the velocity pattern of turbulent flow, they do point to the fact that unlike molecular diffusion and viscosity, eddy diffusion and eddy viscosity are primarily functions of the state of motion of the fluid as described by the Reynolds number and not functions of the physical properties of the system except in so far as they may affect the Reynolds number. For short distances the material transfer in a turbulent stream does not take place by diffusion in the ordinary sense, i.e., the rate of diffusion is not proportional to the concentration gradient and eddy diffusivity depends only on the intensity of turbulence; whereas for longer distances, it depends both on the intensity and the

scale of turbulence. Towle[5] in his direct determination of eddy diffusivity found that it was of the order of a hundred times the molecular diffusivity in case of hydrogen or carbon dioxide diffusing into a turbulent air stream, increasing approximately in proportion to the Reynolds number.

The Two film Theory

Eddy diffusivity in turbulent streams being very much greater than molecular diffusivity generally, the principal resistance to the overall mass transfer process lies in the region through which the material must pass by molecular diffusion. This fact is the basis of the two film theory of Lewis and Whitman[8] according to which transmission of any material across from one phase to the other involves crossing two stagnant fluid films in series by molecular diffusion. The validity of this concept of additivity of resistances has not been tested adequately, but in many instances its application has been successful. It is generally accepted that most of the resistance to mass transfer between phases lies in the interfacial region, although the resistance to transfer by eddy diffusion is not an insignificant fraction of the whole. Since in a process consisting of a number of stages, the overall rate is mainly controlled by the slower ones, the importance of molecular diffusion, or simply diffusion in the study of mass transfer cannot be overemphasized.

Diffusion in Chemical Reaction

Apart from its importance in mass transfer studies, diffusion may be a controlling factor in many catalytic reactions.

In order to react, the reactants have to move by diffusion to the internal surface of the porous catalyst particles to give reasonable conversion rates, which may be insufficient under certain conditions (say, large particle size) to maintain an equal concentration inside and outside the catalyst particle. As a result, the reaction rate is smaller than that corresponding with the intrinsic activity of the catalyst surface. So much so that even in the case of ammonia synthesis where it is generally accepted that the reaction rate is too slow to be retarded by a restricted diffusion rate and where the influence of the particle size on the reaction rate is not observed, the reaction rate may be retarded for this reason under technical conditions. This has been shown by Wagner[9] and by Wheeler[10] from the estimation of the diffusion rate inside the porous catalyst particles. The former pointed out that at high pressure, the transport of the adsorbed molecules or radicles by surface migration might contribute considerably to the diffusion rate. The evidence for this is provided by the work of Kummer and Emmett[11] on exchange experiments between N_2^{30} and N_2^{28} over iron synthetic ammonia catalysts.

Another field in which the study of diffusion has found wide application is the investigation of solution rate and chemical reaction. Danckwerts[12] has shown that the rate of solution depends both on the diffusion coefficient and on the reaction rate constant.

The purpose and scope of the work

It is evident from what has been said that the study of diffusion is very essential in approaching the problem of mass transfer in a more systematic way. Since the diffusivity in gases is much higher than that in liquids, the former does not impose such a great limitation on the overall rate (except in the case of highly soluble gases) as the latter. Moreover, satisfactory methods are available by which diffusivity in gases may be estimated whereas those for liquids are not so reliable since the kinetic theory of liquids is not as well-developed as that of gases. The data for diffusivity in liquids, especially those for gases in liquids, are very scanty in the literature and as far as the author is informed, a convenient method for the measurement of diffusivity of gases in liquids is yet to be reported, although methods for measuring diffusivity of solids or liquids in liquids are fairly established. It has been the purpose of this work to measure the diffusivities of a few gases in liquids and to investigate its relation to mass transfer rates. Systems having fairly wide range of solubilities were chosen - from very slightly soluble hydrogen in water to fairly soluble sulphur dioxide in water. In case of slightly soluble gases where the gas film resistance is not very important, the diffusion coefficients are correlated with liquid film transfer coefficients wherever the latter are available. In the absence of such data, the liquid film transfer coefficients are to be predicted on the basis of experimentally determined values of diffusivity under specific

conditions of mass transfer. The equations of Lewis and Whitman[8], of Higbie[13] and of Danckwerts[12] for mass transfer between gases and liquids are to be compared on the basis of experimentally determined values of liquid film transfer coefficients and the values obtained by substitution in the respective equation of the different terms. It is not intended to extend this work to systems involving the complicating effects of chemical reaction or heat transfer in course of the process of mass transfer although a few such systems are included for the determination of diffusivity.

The object of this work is thus:

(1) Measurement of diffusivity of a few gases in liquids and

(2) Application of experimentally determined values of diffusion coefficients to rate of mass transfer between gases and liquids.

PART II

Section A

PART II

Section A

Theoretical Considerations

Diffusion

If inhomogeneities in concentration exist in a system of miscible substances, the mobile constituents tend to migrate to a region of lower concentration. In the absence of any external force all the components are uniformly distributed throughout the volume in course of time and this phenomenon is called translational diffusion or commonly diffusion. The process is caused by the existence of a thermodynamic free energy gradient in the system and is controlled by factors like temperature, entropy and composition. The evidence for this is born out by the fact that there is no net diffusion across the interface of a solute partitioned between two immiscible solvents. The process is irreversible as a consequence of the second law of thermodynamics.

The diffusion coefficient

In order to measure diffusion quantitatively, it is necessary to define for any substance the diffusion coefficient D which is numerically equal to the quantity of that substance (not dimensionally) which passes perpendicularly through a reference surface of unit area in unit time when the driving force causing this transfer (i.e. the concentration gradiant)

is unity. It is to be noted that the unit in which the quantity of substance is expressed does not affect D which has the dimensions of length squared per time for it cancels out with the unit of quantity in the concentration gradient when consistent units are used throughout. It is apparent, therefore, that D is dependent on the frame of reference to which the process is referred. Experimental measurements are made in a frame of reference fixed with respect to a plane in the system.

Classification of diffusion experiments

The various processes employed for determining D may be divided into three classes depending on the boundary conditions:

(1) Free diffusion: This refers to diffusion between two solutions of different concentrations having initially a sharp boundary between them in a vertical column in which there is no change in composition at the top and at the bottom during the period of observation.

The absorption, the scale and the schlieren methods usually employ free diffusion.

(2) Restricted diffusion: If free diffusion is continued, eventually concentration changes begin to occur at one or both ends of any column of finite height and the process is then referred to as restricted diffusion.

The conductivity method employing a Tiselius type of diffusion cell is an example of restricted diffusion.

(3) Steady-state diffusion: If the concentration at the two ends of a diffusion column is maintained constant, say by allowing them access to reservoirs of appropriate concentrations, a steady state is eventually established in which the concentration distribution throughout the column does not change with time. Under such conditions the diffusion flow is constant at each height in the column and the process is known as steady-state diffusion. If D is independent of concentration, the concentration of the solution varies linearly with the height of the column.

The work of Clack [50], and as a first approximation the porous diaphragm method exemplify steady-state diffusion.

The integral and differential diffusion coefficients

Since the diffusion coefficient is generally a function of concentration, it is necessary to define it further into two categories, viz., the differential diffusion coefficient which is the value at a specific concentration and the integral diffusion coefficient which is the average value over a specified concentration range. Obviously, the former is the one having greater theoretical significance.

Fick's laws

It is only appropriate to start a theoretical treatment of the process of diffusion with the enunciation of Fick's laws[45] which relate the rate of flow of a diffusing substance with the concentration gradient causing that flow. Since in inter-diffusion at least two substances are involved, generally there

is more than one diffusion equation, one for each substance involved. In the case of a two-components system, two equations are necessary, but as the magnitude of the rate of flow of both the components is generally equal, the difference being only in the direction which is opposite, the second equation is not considered seperately.

If Q be the amount of a substance passing perpendicularly through a reference plane of unit area in the direction x and c be the concentration of the same substance before diffusion takes place, then Fick's first law may be stated as:

$$Q = -D \cdot \frac{\partial c}{\partial x} \quad \ldots\ldots\ldots (1)$$

for unidirectional diffusion where D is the diffusion coefficient defined earlier. In C.G.S. units, Q has the dimensions of gm. $cm.^{-2}$ $sec.^{-1}$, c of gm. $cm.^{-3}$, and x is in cm. Therefore D has the dimensions of $\frac{\text{gm. cm.}^{-2} \text{ sec.}^{-1} \text{ cm}}{\text{gm. cm.}^{-3}} = \text{cm.}^{2} \text{ sec.}^{-1}$ and is independent of the unit of quantity chosen for expressing Q provided that consistent units are used throughout.

The equation implies that D is constant for a given medium, temperature and pressure which is only approximately true. It has been shown that in general D is a function of temperature and concentration and possibly also of concentration gradient (14, 15, 16). Since the equation is derivable from the osmotic theory, a limiting value of D at infinite dilution is to be expected and the relation therefore is recognised as a typical limiting law.

In order to measure D with the help of equation (1) it is

necessary to measure Q as well as $\frac{\partial c}{\partial x}$ which requires the establishment of a steady-state in which the concentration gradient is constant. In many cases encountered in practice, it is not easy to maintain a steady state and it becomes essential to measure the change of concentration with time at any point along the diffusion column. In other words, it is necessary to observe the increase in the amount of the diffusing substance within a volume element bounded by two parallel planes of unit area situated at x and $x + dx$ in time t. Application of equation (1) then leads us to:

$$(Q)_x - (Q)_{x+dx} = D\left[\left(\frac{\partial c}{\partial x}\right)_{x+dx} - \left(\frac{\partial c}{\partial x}\right)_x\right]$$

$$= D\left(\frac{\partial^2 c}{\partial x^2}\right) . dx + \ldots\ldots\ldots \text{ (Taylor's Theorem).}$$

Dividing throughout by the volume $dx.1cm.^2$ of the element, we obtain for the increase of concentration with time in the limit $x \longrightarrow 0$:

$$\frac{\partial c}{\partial t} = D.\frac{\partial^2 c}{\partial x^2} \quad \ldots\ldots\ldots\ldots (2)$$

which is Fick's second law derived on the assumption that D is a constant.

If diffusion occurs in an arbitrary direction, corresponding expressions for Y and Z co-ordinates must be added to the right hand sides of equations (1) and (2) and in that case they become:

$$Q = -D\left(\frac{\partial c}{\partial x} + \frac{\partial c}{\partial y} + \frac{\partial c}{\partial z}\right) \quad \ldots\ldots\ldots\ldots (3)$$

$$\text{and } \frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right) \quad \ldots\ldots\ldots (4)$$

By employing adequate initial and boundary conditions, equations (1), (2), (3) and (4) can be solved.

Evaluation of D when it is a function of concentration

Since D is generally a function of concentration, we have to treat D as a variable while deriving a relation for the change of concentration with time. Equation (1) still remains unchanged, but equation (2) becomes:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D.\frac{\partial c}{\partial x}\right) \quad \ldots\ldots\ldots \quad (5)$$

instead and may be written as

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} + \left(\frac{\partial D}{\partial c}\right)\left(\frac{\partial c}{\partial x}\right)^2 \quad \ldots\ldots\ldots \quad (6)$$

As before when the increase in the amount of the diffusing substance within a volume element bounded by two parallel planes of unit area situated at x and $x + dx$ in unit time is observed, we have,

$$(Q)_x - (Q)_{x+dx} = -\left(D.\frac{\partial c}{\partial x}\right)_x + \left(D.\frac{\partial c}{\partial x}\right)_{x+dx}$$

$$= -\left(D.\frac{\partial c}{\partial x}\right)_x + (D)_x \left(\frac{\partial c}{\partial x}\right)_{x+dx} + \left(\frac{\partial D}{\partial c}\right) .dc \left(\frac{\partial c}{\partial x}\right)_{x+dx} \quad \ldots\ldots\ldots \quad (7)$$

where dc is the concentration difference corresponding to the distance dx.

When D shows a marked dependence on concentration, one has to use equations (5) or (7), but these are very inconvenient to apply in most cases. A simpler way is to use a very small concentration difference in the system, keeping the average concentration constant in the volume element under consideration, thus keeping D and $\frac{\partial D}{\partial c}$ unchanged. Then the differential coefficients with respect to x will change by amounts approximately

proportional to the change of concentration difference and with decreasing dc, the third term on the right hand side of equation (7) will decrease as $(dc)^2$ while the preceding terms decrease as dc only and may be neglected. If the variation of D within the concentration range under consideration is small compared with D. the second term which contains $\frac{\partial D}{\partial c}$ may also be neglected as the concentration differences will be very small. Thus differential diffusion coefficients may be determined employing equation (2) when a sufficiently small concentration range is involved. If, however, D varies with concentration as well as concentration gradient (14, 15, 16), i.e., when $D = f\ (c_1 \frac{dc}{dx})$ e.g. in the case of highly assymetric particles or highly concentrated solutions, both Q and $\frac{dc}{dx}$ must be measured at a known value of c which means the establishment of steady state and employment of equation (1).

Relation between integral and differential diffusion coefficients

As a consequence of the variation of diffusion coefficient with concentration it becomes necessary to classify it as integral and differential coefficients as noted earlier and the two may be related as shown below.

Now the differential diffusion coefficient D is given by equation (1), which may be written as:

$$D = -Q / \frac{\partial c}{\partial x} \quad \ldots\ldots\ldots\ldots (8)$$

while the corresponding integral coefficient $\bar{D}$ is given by the equation:

$$\bar{D} = -Q / \frac{c_1 - c_{11}}{\ell} \quad \ldots\ldots\ldots (9)$$

These two equations may be combined to give the relation between D and $\bar{D}$:

$$\bar{D} = D/\frac{\partial x}{\partial c} \cdot \frac{\ell}{c_I - c_{II}}$$

$$= \frac{1}{c_{II} - c_I} \int_{c_I}^{c_{II}} D.dc \quad \ldots\ldots\ldots \quad (10)$$

corresponding to the concentration interval from c_I to c_{II}.

Diffusion accompanied by a change in volume

In cases where diffusion is accompanied by a change in volume i.e. when the partial specific volume of solution is not zero, a flow of solvent takes place and a correction is required of Fick's equation while determining D in the moving frame of reference. Equation (1) in such a case becomes:

$$\frac{\partial v}{\partial t} = -D_S \frac{\partial c}{\partial x} - c \cdot \frac{\partial v}{\partial t} \quad \ldots\ldots\ldots \quad (11)$$

in which $\frac{\partial v}{\partial t}$ is the rate of transfer of solute across a plane of unit area at concentration c, $\frac{\partial v}{\partial t}$ is the rate of change of volume of the residual solution and D_S is the diffusion coefficient.

Since $\frac{\partial v}{\partial t} = \frac{\partial v}{\partial q} \cdot \frac{\partial v}{\partial t}$. we can write

$$D_S = -Q \left(1 + c.\frac{\partial v}{\partial q}\right) \left(\frac{\partial c}{\partial x}\right)^{-1} \quad \ldots\ldots\ldots \quad (12)$$

If q is expressed in gms., $\frac{\partial v}{\partial v} = \bar{v}$, the partial specific volume and equation (12) becomes:

$$D_S = D(1 + c\bar{v}) \quad \ldots\ldots\ldots \quad (13)$$

If the concentration of the residual solution is not uniform, a mean value of $\bar{v}$ may be used as a first approximation or the

curve of c vs. $\bar{v}$ is plotted and integrated. If D depends on concentration, equation (11) should be derived from equation (5) instead and further assumptions are necessary to solve the relation.

Variation of D with temperature

The study of the situation regarding the variation of D with temperature has been less satisfactory so far. On the basis of the scanty data available it has usually been represented by the equation:

$$\frac{D_2}{D_1} = 1 + \alpha (T_2 - T_1) \quad \ldots\ldots\ldots\ldots \quad (14)$$

until relatively recently, indicating a linear variation of D with absolute temperature. Taylor[17], however, obtained a linear plot of log. D vs. $\frac{1}{T}$ utilising the data of Cohen and Bruins[18] which is to be expected from the relation of Eyring[19]:

$$D = \lambda^2 \frac{kT}{h} . \exp. \frac{-\Delta F}{RT} \quad \ldots\ldots\ldots\ldots \quad (15)$$

The exponential variation of D with T is also expected on the basis of the measurement of variation of viscosity with temperature by Ewell and Eyring[19] since the two are related, and of diffusivity with temperature by Smith and Starrow[20]. Until sufficient information on the variation of diffusivity with temperature is available, Eyring's equation seems to represent the situation best and has been found quite satisfactory according to the concept of holes in liquids.

The Steady State

Since in this work we shall be dealing mainly with diffusion in stationary (steady) or quasi-steady states, it is necessary to give a detailed account of the same and derive relations leading to the experimental determination of diffusivities by these methods.

In the steady state, the concentration is maintained constant at the two ends of the diffusion column, i.e.,

$$\frac{\partial c}{\partial t} = 0 \quad \ldots\ldots\ldots\ldots \quad (16)$$

For unidirectional diffusion, we substitute (16) into (2) to give:

$$D.\frac{\partial^2 c}{\partial x^2} = 0 \quad , \text{ i.e., } \frac{\partial c}{\partial x} = \text{constant;}$$

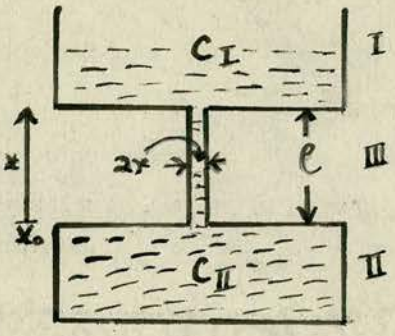
in other words,

$$C = C_0 + C_1 x_1 \quad \ldots\ldots\ldots \quad (17)$$

which means that a constant concentration gradient and a linear distribution of concentration exist in such a system if D can be treated as constant. For the determination of D we have to measure Q as well as $\frac{\partial c}{\partial x}$ in such a case and an arrangement as shown in the figure is suitable for the purpose.

Two large reservoirs I and II containing solutions at concentrations C_I and C_{II} (which remain sensibly constant during the period of observation) are connected by means of a comparatively narrow tube III of radius r and length l. After a certain time, depending on r and l, a steady state will be established, varying but slowly with time. If the solutions in the two reservoirs are maintained uniform by stirring or

otherwise, the concentration distribution in III then will be as shown in the figure at various times.

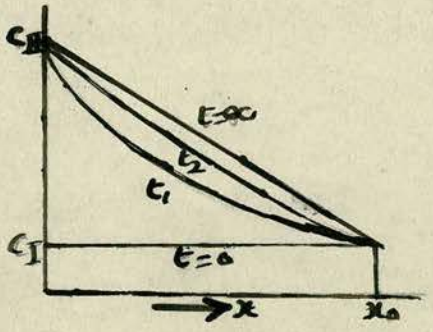


Then $\frac{\partial c}{\partial x} \approx -\frac{\Delta c}{\ell} = \frac{c_I - c_{II}}{\ell}$ ..... (18)

and $Q = \frac{S}{\Delta t \cdot \pi r^2}$ ..... (19)

where S is the increase in the amount of diffusing substance in I ($c_I < c_{II}$).

Hence, $D = \frac{S}{\Delta t \cdot \pi r^2} \cdot \frac{\ell}{c_{II} - c_I}$ ..... (20)



If D is concentration-dependent, the stationary concentration distribution corresponding to $t = \infty$ is not linear. In such a case D obtained by (20) is the integral diffusion coefficient

over the range involved. If one has to measure differential diffusion coefficients at different concentrations, the concentration distribution during the steady state along the column must be determined. Then D can be measured as a function of x or of C since it is inversely proportional to $\frac{\partial c}{\partial x}$. Otherwise differential diffusion coefficient may be obtained with the help of equation (10) in conjunction with the measured integral coefficient.

A good example of steady state diffusion is afforded by the diffusion of a vapour of a volatile liquid at the bottom of a container into air outside it (21). For instance, if some volatile liquid, say, ether, is placed at the bottom of a vertical cylinder, the vapour diffuses from the surface of the liquid to the atmosphere above the open end of the cylinder. If the cylinder is sufficiently long and not too wide (to avoid convection currents) and the concentration of the vapour is maintained zero at the open end by removing the air continuously above the top of the cylinder by convection current or otherwise, a steady state will be established to a sufficient approximation after a certain length of time when the vapour will diffuse into the atmosphere at a constant rate. The concentration of the vapour at the liquid surface in such a case will be determined by the vapour pressure of the liquid at the temperature of the experiment and l in equation (20) will correspond to the length from the surface of the liquid to the open end of the cylinder. By measuring

the amount of liquid evaporating in time t, D can be calculated by the application of equation (20).

The Quasi-Stationary State

In the example given above, the steady state, however, is not maintained to the strictest sense of the term because of the fall of liquid level with time due to evaporation and consequently change in concentration distribution with time (due to increasing ℓ). Such cases are very important in the experimental determination of D and are said to involve quasi-stationary state diffusion. Equation (16) in such a case takes the form:

$$\frac{\partial c}{\partial t} \approx 0 \quad \ldots\ldots\ldots\ldots \quad (21)$$

implying that although the concentration gradient may be assumed to be constant with sufficient accuracy, it is not independent of time. By far the most important application of this principle lies in the diaphragm cell method.

The method consists in having two solutions of different concentrations in two compartments of a diffusion cell into which it is divided by means of a porous diaphragm, usually of sintered glass. The concentrations in the two compartments are maintained uniform by density or mechanical stirring and it is assumed that the process of diffusion is confined to the pores of the sinter in which a constant concentration gradient is maintained after the establishment of a quasi-stationary state (which requires a preliminary period of non-steady diffusion)

to sufficient approximation. If A be the effective cross-section of the diaphragm, L its effective length (i.e. thickness), and C_1 and C_2 the concentrations of solutions in the two compartments ($C_1 < C_2$); then equation (1) can be written as

$$Q = A.\ (C_2 - C_1)\ \frac{D}{L}. \quad \ldots\ldots\ldots\ldots\ (22)$$

When a quasi-stationary state is established, the concentration gradient within the diaphragm will be constant to sufficient approximation, i.e., $\frac{\partial c}{\partial x} \approx \frac{C_1 - C_2}{L}$, while it will not be independent of time.

In such a case when V is the volume of either compartment (equal), the rate of change of concentration because of diffusion will be given by:

$$\frac{dc_1}{dt} = \frac{-dc_2}{dt} = \frac{Q}{V} = A.\ (C_2 - C_1) \cdot \frac{D}{VL} \quad \ldots\ldots\ldots\ (23)$$

[substituting from equation 22.]

In the general case of unequal volumes of the two compartments, if V_1 be the volume of one containing solution of concentration C_1 and V_2 be that containing solution of concentration C_2, one similarly obtains:

$$V_2 dc_2 + \left(\frac{DA}{L}\right)(C_2 - C_1)\ dt = 0 \quad \ldots\ldots\ldots\ (24a)$$ After
$$V_1 dc_1 + \left(\frac{DA}{L}\right)(C_1 - C_2)\ dt = 0 \quad \ldots\ldots\ldots\ (24b)$$ transposition

Equations 24 a and b may be combined to give:

$$\frac{d(C_2 - C_1)}{C_2 - C_1} + \frac{D.A.}{L}\left(\frac{1}{V_1} + \frac{1}{V_2}\right) dt = 0 \quad \ldots\ldots\ldots\ (25)$$ after

dividing by V_2 and V_1 respectively throughout and equating.

On integration, we get

$$\log_e \frac{(C_1 - C_2)_f}{(C_1 - C_2)_i} = - K.D.t. \quad \ldots\ldots\ldots (26)$$

where $K = \frac{A}{L}\left(\frac{1}{V_1} + \frac{1}{V_2}\right)$ ..... (26a)

$(C_1 - C_2)_f$ and $(C_1 - C_2)_i$ refer to final and initial concentration differences between the solutions of the two compartments during the time interval t, respectively. Equation (26) may be rewritten as:

$$D = \frac{1}{K.t} \cdot \log_e \frac{(C_1 - C_2)i}{(C_1 - C_2)_f}$$

$$= \frac{1}{Kt} \cdot \log_e \frac{C_{f1} + C_{f2} \times \frac{V_2}{V_1}}{C_{f1} - C_{f2}} \quad \ldots\ldots\ldots\ldots (27)$$

where C_{f1} and C_{f2} are the final concentrations in the two compartments of volumes V_1 and V_2 respectively after diffusion has proceeded for t seconds from a solution of concentration C_0 in V_1 to pure solvent in V_2. ($C_0 = C_{f1} + C_{f2} \cdot \frac{V_2}{V_1}$ in this case).

Since it is not possible to measure $\frac{A}{L}$ directly, the usual practice is to determine K by employing a substance of known diffusion coefficient and the method is a relative one. $\frac{A}{L}$ can then be calculated from the relation given above if V_1 and V_2 are known.

Barnes [22] has treated the problem of diaphragm cell without the assumption of a quasi-stationary state i.e. when the rate of change of concentration in the compartments is not sufficiently slow compared with the establishment of an almost

linear concentration distribution within the diaphragm. Under ordinary experimental conditions, the additional terms obtained by him in the relation describing the change of concentration with time in a compartment are not very significant and may be neglected.

The relative error in concentration measurement $\frac{\delta c}{c}$ causes a relative error in measured D and the latter may be obtained by differentiating equation (27). By employing this method, Stokes[23] showed that even when a 2N solution of potassium chloride is allowed to diffuse into a 1N solution of potassium chloride, there may be a tenfold magnification of analytical errors, while if the initial concentrations are made closer to obtain differential diffusion coefficients directly, the error becomes much more serious. However, if the initial concentration in one of the compartments is zero, the relative error in integral diffusion coefficient rises only slowly as the run proceeds and scarcely exceeds $2\frac{\delta c}{c}$ for runs of normal duration.

In the latter case, equation (10) assumes the form:

$$\bar{D} = \frac{1}{c}\int_0^c . D. dc \quad \ldots\ldots\ldots (28)$$

[here $C_{II} = c$ and $C_I = o$.]

and may be differentiated to yield:

$$D = \bar{D} + C.\frac{d\bar{D}}{dc}$$

$$\text{or} \quad D = \bar{D} + \frac{\sqrt{c}}{2} \cdot \frac{d\bar{D}}{d\sqrt{c}} \quad \ldots\ldots\ldots (29)$$

The slopes $\frac{d\bar{D}}{dc}$ or $\frac{d\bar{D}}{d\sqrt{c}}$ can be obtained graphically and differential values obtained from measured integral coefficients.

Both Gordon[24] and Stokes[23] have verified equation (10) experimentally which confirms the establishment of a quasi-stationary state within the diaphragm as equation (10) is based on that assumption. The latter, in addition, obtained excellent agreement between observed and calculated integral coefficients with the help of equation (29) and measured differential values.

The Stokes-Einstein equation

On the basis of the osmotic theory, Einstein[25] derived his fundamental equation for diffusion in liquids which leads to the famous Stokes-Einstein equation when applied to spherical molecules diffusing into a medium of comparatively small molecular dimensions. Although the equation is valid only for ideal dilute solutions or at very low concentrations in real systems where the osmotic law is obeyed, it is considered necessary to give a brief account of the same as it leads to some very important relationships incorporating the relation between diffusivity, viscosity of the medium, temperature and geometry of the diffusing molecule.

If C be the concentration and p the osmotic pressure at the plane x in a diffusion cylinder of uniform cross-sectional area A, the force on the solute particles at the plane x will be: Ap. in the positive and negative x -directions when only unidirectional diffusion is considered.

Similarly, at the plane $x + \delta x$, the force on the solute particles in positive and negative x-directions will be: $A(p + \delta p)$.

Therefore, the resultant force on the solute particles in the volume element $A\delta x$ bounded by the planes x and $x + \delta x$ will be $-A\delta p$ in the positive x-direction, i.e. in any plane, the force on the solute particles present in unit volume in the positive x-direction is given by the osmotic pressure gradient $-\frac{A\delta p}{A\delta x} = -\frac{\delta p}{\delta x}$; the negative sign implying that the diffusion takes place in the direction of decreasing osmotic pressure.

For an ideal solution at high dilutions, we have,

$$p = CRT \text{ in usual notations} \quad \ldots\ldots (30)$$

$$\text{i.e. } \frac{\delta p}{\delta x} = RT \cdot \frac{\delta c}{\delta x} \quad \ldots\ldots\ldots (31)$$

when C is expressed in moles per c.c., the number of solute particles in unit volume is NC where N is the Avogadro number.

Therefore, the force acting on each solute particle:

$$f_1 = -\frac{RT}{NC} \cdot \frac{\delta c}{\delta x} \quad \ldots\ldots\ldots (32)$$

This force tends to drive the solute molecules in the direction of lower concentration and therefore to wipe out the concentration gradient. It is opposed by the force of friction between the solute molecules and the solvent. If the solute molecules are large, this force of friction may be approximately calculated from Stoke's law[26] which gives as the opposing

force,

$$f_2 = 6\pi\eta r \overset{u}{v} \quad \ldots\ldots\ldots\ldots (33)$$

where η is the viscosity of the medium (solvent), r and v are the radius and the velocity respectively of the diffusing molecule (i.e. solute, assumed spherical).

At equilibrium the two forces given by equations 32 and 33 are equal, so that,

$$6\pi\eta r u = -\frac{RT}{N} \cdot \frac{1}{C} \cdot \frac{\partial c}{\partial x} \quad \ldots\ldots\ldots (34)$$

$$\text{or,} \quad uc = -\frac{RT}{N} \cdot \frac{1}{6\pi\eta r} \cdot \frac{\partial c}{\partial x} \quad \ldots\ldots\ldots (35)$$

But uc = the total number of molecules crossing a unit area in unit time $= -D \cdot \frac{\partial c}{\partial x}$ from equation 1. $\ldots\ldots\ldots$ (36)

$\therefore$ combining (35) and (36) we get,

$$D = \frac{RT}{6\pi\eta N r} \quad \ldots\ldots\ldots (37)$$

the equation, commonly known as the Stokes-Einstin equation. It is apparent that the equation is valid only for the systems obeying Stoke's law as well as vant Hoff's law of osmotic pressure.

In spite of these limitations, the above leads to some very important relationships which are as follows:

(i) At the same temperature, the diffusion coefficient of the same solute in different solvents should be inversely proportional to the solvent-viscosity i.e. $D\eta$ should be constant for constant T.

(ii) At the same temperature, the diffusion coefficient in the same solvent of different solutes should be inversely proportional to the solute-radius i.e. Dr should be constant for constant T.

(iii) For any system, the product $\frac{D\eta}{T}$ should be constant provided that r does not vary much with temperature (as is usually the case).

The Eyring relation

Recently Eyring[19] has applied his theory of absolute reaction rates to the process of diffusion and has obtained the following relation:

$$D = \frac{\lambda_1}{\lambda_2 \lambda_3} \cdot \frac{kT}{\eta} \quad \ldots\ldots\ldots (38)$$

where λ_1, is the perpendicular distance between two neighbouring layers of molecules sliding past each other;

λ_2 is the distance between neighbouring molecules in the direction of flow;

λ_3 is the intermolecular distance in the plane normal to the direction of motion;

k is a constant;

and η is the viscosity of the medium.

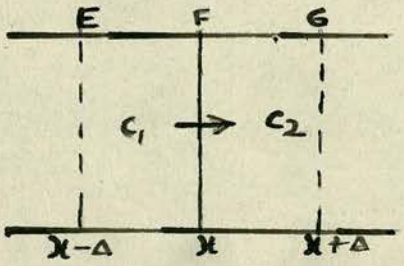
It is seen that the factor $\frac{R}{6\pi Nr}$ in the Stokes-Einstein equation is replaced by k. $\frac{\lambda_1}{\lambda_2 \lambda_3}$ in the Eyring equation. These two factors are of the same order of magnitude and from the data available, it is difficult to say which one is preferable. A particle as large as gold sol obeys the Stokes-

Einstein equation closely, but the Eyring relation is probably nearer the truth when diffusion of molecules of similar sizes, e.g., in self-diffusion, is considered.

Mean displacement of a diffusing particle

It will be of interest to estimate to what distance a diffusing particle will travel during a given time. As the molecular velocities differ so much, a mean value has to be obtained and will be particularly useful in calculating the amount of solute passed into solution given a certain time of contact. From such calculations, the time of contact may be varied to give maximum advantage.

Let Δ be the mean displacement of molecules or particles in the direction x, parallel to the axis of a cylinder of uniform cross-section A in which diffusion is taking place, in a short interval of time t.



Let planes E, F, and G be separated by a distance Δ and C_1 be the mean concentration of the solute in the space between planes E and F, C_2 that between planes F and G ($C_1 > C_2$).

Since displacements in all directions are equally probable, only half of the molecules have positive displacements, and in time t, the mean displacement in the positive

$$x\text{-direction} = \frac{\Delta}{2}$$

and the mean displacement in the negative

$$x\text{-direction} = \frac{\Delta}{2}.$$

Therefore, the amount of solute crossing plane F in time t:

$$q = \frac{\Delta}{2} \cdot A.C_1 - \frac{\Delta}{2} \cdot A.C_2 = \frac{\Delta}{2} \cdot A.(C_1 - C_2) \ldots\ldots (39)$$

since Δ is small.

$$\frac{\partial c}{\partial x} = \frac{-(C_1 - C_2)}{\Delta} \ldots\ldots\ldots\ldots (40)$$

From (39) and (40) we get,

$$q = \frac{-\Delta^2}{2} \cdot A \cdot \frac{\partial c}{\partial x} \ldots\ldots\ldots (41)$$

When the amount Q passing through unit area in plane F in unit time is considered, equation (41) becomes,

$$Q = \frac{-\Delta^2}{2t} \cdot \frac{\partial c}{\partial x} \ldots\ldots\ldots (42)$$

But from equation (1) we have, $Q = -D \cdot \frac{\partial c}{\partial x}$, and leads to:

$$D = \frac{\Delta^2}{2t} \ldots\ldots\ldots\ldots (43)$$

known as Einstein's general law of the particle. When the Δ s are not all equal, as is the case, equation (43) should be written as:

$$D = \frac{\bar{\Delta}^2}{2t} \ldots\ldots\ldots\ldots (44)$$

giving the average of the squares of displacements.

The equation is valuable in estimating the depth to which a diffusing substance will penetrate into a given medium during time t. Furth[27] has shown a remarkable agreement between

the observed and calculated displacements on the basis of Perrin's[28] measurements with gamboge particles.

Diffusion from a spherical shell and from a hollow cylinder

So far diffusion has been considered through a constant cross-section of a column only. In practice, cases are encountered when diffusion takes place from a spherical shell as in mass transfer involving bubbles or from a hollow cylinder. In the former case, the cross-section for diffusion increases with the square of the radius and when a substance is diffusing in the direction of increasing radius, concentration varies inversely as the radius for $\frac{\partial c}{\partial r}$ varies as $\frac{1}{r^2}$. For steady-state diffusion, Barrer[29] has obtained following expressions in the two cases.

(i) The Spherical Shell: If the shell extends from radius r_1 to r_2 and if at r_1 and r_2 the stationary concentrations C_1 and C_2 are maintained, the steady-state concentration C at any value of r is given by:

$$C = C_1 + \frac{r_2 (r - r_1)}{r (r_2 - r_1)} (C_2 - C_1) \quad \ldots\ldots\ldots (45)$$

and the flow per unit time per unit area of the shell is given by,

$$\left(\frac{\partial c}{\partial r}\right)_{r = r_2} = (C_2 - C_1) \cdot \frac{r_1}{r_2} \cdot \frac{1}{(r_2 - r_1)} \quad \ldots\ldots\ldots (46)$$

In the limiting case, when $r_2 - r_1 = \delta \ll r_1$, equation (46) passes into the expression for a plane layer:

$$\frac{\partial c}{\partial r} \approx \frac{C_2 - C_1}{\delta} \quad \ldots\ldots\ldots (47)$$

which means that if the thickness is small compared with radius, the layer can be treated as a plane to sufficient approximation.

The quantity Q diffused in time t is given by:

$$Q = 4\pi D.\ (C_1 - C_2)\ \frac{r_1 r_2}{r_2 - r_1}\ .\ t \quad \ldots\ldots\ldots\ (48)$$

(ii) <u>The Hollow Cylinder</u>: For this case, one obtains,

$$C = \frac{C_1 - C_2}{\log r_1 - \log r_2}\ \log r + \frac{C_2 \log r_1 - C_1 \log r_2}{\log r_1 - \log r_2} \quad \ldots\ldots\ldots\ (49)$$

$$\text{and } \frac{\partial c}{\partial r} = \frac{C_1 - C_2}{\log r_1 - \log r_2}\ .\ \frac{1}{r} \quad \ldots\ldots\ldots\ (50)$$

when $r_2 - r_1 = \delta \ll r_1$, as before,

$$\frac{\partial c}{\partial r} \approx \frac{C_2 - C_1}{\delta} \quad \ldots\ldots\ldots\ (51)$$

And the quantity Q diffusing through unit length of the cylinder in time t is given by:

$$Q = \frac{2\pi D\ (C_2 - C_1)\ t}{\log r_2 - \log r_1} \quad \ldots\ldots\ldots\ (52)$$

PART II

Section B

PART II

Section B

Diffusion and Mass Transfer

Diffusion has been considered so far from a purely physical point of view only. In this section an attempt will be made to correlate diffusivity with mass transfer rates with special reference to the unit operation of gas absorption. While doing so, the consideration will be confined to the physical process of mass transfer without the complicating effect of chemical reaction or heat transfer within the system.

The Theory of Lewis and Whitman

As noted before, the earliest theory describing the process of absorption is that of Lewis and Whitman[8] incorporating the following ideas:

(1) Existence of two fluid films at the interface assumed to be stagnant or in streamline flow.

(2) Passage of material through these films only by stationary molecular diffusion.

(3) Assumption of complete homogeneity in the bulk of the fluids, the resistances encountered in these phases being incorporated in the respective equivalent film thicknesses.

(4) Absence of resistance to transfer at the interface, and

(5) Principle of additivity of resistances.

On this basis, they obtained:

$$R = k_L (C_i - C) = k_G (p - p_i) \quad \ldots\ldots\ldots (53)$$

where R is the rate of mass transfer, k_L and k_G are the liquid and the gas film coefficients respectively, i's refer to conditions at the interface and small letters to those in the bulk of the fluids. In terms of overall coefficients:

$$R = K_G (p - p_e) = K_L (C_e - C) \quad \ldots\ldots\ldots (54)$$

where K_G and K_L are overall mass transfer coefficients expressed in terms of partial pressure and concentration respectively and e's refer to conditions in equilibrium with bulk phases in the other phase. If Henry's law is obeyed, equations (53) and (54) lead to:

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{H}{k_L} \quad \ldots\ldots\ldots\ldots (55)$$

and

$$\frac{1}{K_L} = \frac{1}{k_1} + \frac{1}{Hk_G} \quad \ldots\ldots\ldots\ldots (56)$$

where H is the Henry's law constant, $\frac{1}{K_G}$ and $\frac{1}{K_L}$ are overall resistances in terms of partial pressure and concentration respectively, $\frac{1}{k_G}$ and $\frac{1}{Hk_G}$ gas film resistances, $\frac{1}{k_L}$ and $\frac{1}{Hk_L}$ liquid film resistances.

It is evident that if H is large, i.e., if the solubility of the gas in the liquid is low, the rate is controlled by liquid film resistance and if H is small, the rate is controlled

by gas film resistance. For gases of intermediate solubility, both film resistances are to be taken into account. For gases of sufficiently low solubilities, it follows, the gas film resistance is negligible and need not be taken into account in calculations. In order to study the mechanism of mass transfer in the liquid phase, therefore, it is necessary to choose systems of comparatively small gas solubilities. In such a case, comparison of equation (53) with (1) will show:

$$k_L = \frac{D}{\delta} \quad \ldots\ldots\ldots \quad (57)$$

where D is the diffusivity of the gas in the liquid and δ is the equivalent liquid film thickness. If both D and k_L be known or experimentally measured, δ can be calculated to examine the implications of the Lewis-Whitman theory.

The Penetration Theory

It was Higbie[13] who first criticised the Lewis-Whitman theory on the following ground:

(1) Since at the instant when the gas and the liquid are brought together the liquid film contains no gas, a certain time is necessary for the penetration of the liquid film by the gas before a steady state is established. This penetration period in certain types of absorption equipment may exceed the time of contact and invalidate the predictions of the film-mechanism.

(2) The above demands that the shorter the period of exposure, the greater the rate of mass transfer. Experiments, however, showed progressively greater deviation from this behaviour

as the period of contact was shortened indicating the presence of some sort of extra resistance at the surface. This casts doubt as to the establishment of equilibrium at all the points of the interface between the two phases.

(3) In the three types of absorption equipment considered, evidence was presented to show that the liquid was effectively still in all the cases and exposed only for a limited period due to systematic surface renewal.

A new mechanism was proposed whence it was contended that although in absorption the laminar layer is always present, the liquid surface is continually renewed according to some mathematical relationship. The rate of passage of the gas into the liquid surface is not infinitely rapid and therefore it is quite probable that the steady-flow conditions are never reached in conventional absorption equipments. From these considerations, the following relationships were proposed:

$$R = 2 (C_i - C) \sqrt{\frac{D}{\pi t_e}} \quad \ldots\ldots\ldots\ldots (58)$$

$$\text{and} \quad k_L = 2 \sqrt{\frac{D}{\pi t_e}} \quad \ldots\ldots\ldots\ldots (59)$$

where t_e is the time of contact. He also considered the probability of the gas undergoing a "first order process" while passing through the surface on the assumption of the absence of equilibrium at the phase boundary. He found the "first order process" analysis as consistent with the then existing data on periodsof ten seconds or more as his own penetration theory incorporating non-stationary diffusion.

The Theory of Danckwerts

Since existing data fitted quite well with the film theory, Higbie's ideas were not considered very significant until Danckwerts[12] referred to them in connection with his proposal for a new mechanism of gas absorption based on similar reasoning. The latter contended that it is very likely that the liquid at the surface is continually displaced by fresh liquid carried to the surface by turbulent eddies. It was further assumed that the probability of replacement of a surface element is the same regardless of its age, i.e., a statistical distribution was attributed to the periods for which an element of liquid stayed at the interface. The element, however, is assumed to absorb at the same rate as a stagnant surface during its exposure. If S be the rate of surface renewal, i.e., the fraction exposed per unit time, according to Danckwerts:

$$R = (C_i - C)\sqrt{DS} \quad \ldots\ldots\ldots (60)$$

and $$k_L = \sqrt{DS} \quad \ldots\ldots\ldots (61)$$

For non-reacting solutions, Danckwerts and Kennedy determined S to be 0.8/ second.

Comparison of the theories of Lewis-Whitman, Higbie and Danckwerts

It is interesting to note, however, that the theories of Lewis and Whitman, Higbie, and Danckwerts although different in their way of derivations lead to closely similar predictions. The reason for this lies in the fact that the terms in their equations which can be measured directly with sufficient

precision are identical, while those which are fundamentally different cannot or have not been measured with sufficient precision up to the present to prove or disprove one or the other. All of these mechanisms allow of a thin film of liquid at the interface but differ in the rate of its renewal which is nil for the first, systematic for the second and random for the last. While Lewis and Whitman visualise a turbulent core beneath a stagnant layer, Higbie and Danckwerts maintain the liquid to behave as a still one as far as the process of absorption is concerned. The most important difference, however, lies in the fact that the Lewis - Whitman model assumes the instantaneous establishment of equilibrium at the interface giving rise to steady state diffusion whereas the latter models maintain an unsteady state to exist initially which may be continued because of surface renewal. That is to say, to start with, at least, the absorption takes place on a fresh surface. This is the weakest point of the film-mechanism as experiments on diffusion show an initial period required for the establishment of equilibrium before a steady state is reached. It must be added, however, if the rate of surface renewal is nil or sufficiently slow, the steady state will exist after an initial penetration period, the relative importance of the two depending on their relative magnitudes.

The limiting factor in the Lewis - Whitman mechanism is the thickness of the stagnant liquid film while that in the later models is the time of contact. Both of these

conceptions are quite compatible with the observations, the difference lying only in the way of explanation. All these theories agree as to the principle of additivity of resistances, if existent.

'First order process' theory

The idea of the gas undergoing a 'first order process' at the interface even in the case of non-reacting systems is not entirely improbable. In fact, the kinetic theory demands that there should be a definite upper limit to the rate at which initial absorption takes place depending on its temperature and pressure and the area of the liquid surface. Miyamoto[30] derived an equation based on the assumption that only the molecules whose velocity-components normal to the surface is higher than a critical value can enter the liquid surface. His experimental results on absorption agreed with that equation. As noted before, Higbie also found this 'first order process' analysis applicable to his results. Matsuyama[31] carried out some experiments on the absorption of carbon dioxide, sulphur dioxide and hydrogen sulphide in a jet type of absorption column with contact time of about .01 second to find that his results agreed approximately with the theory only after allowance was made for the occurence of a first order process. Even Danckwerts and Kennedy[12] on the basis of their measurements of transient absorption rates of carbon dioxide in water were forced to conclude that there was a substantial surface resistance to the absorption of carbon dioxide into water, the concentration of dissolved

carbon dioxide at the surface being less than the saturation value. In such a case there was a definite upper limit to the rate of absorption $K_S C^*$, where K_S is the "surface mass transfer coefficient" and C^* is the saturation concentration of dissolved gas in liquid. A low accommodation coefficient was accounted for such surface resistance returning to the idea of Miyamoto.

Implications of the various absorption mechanisms

Coming to the quantitative implications of the three models, a glance at equations (57), (59) and (61) will show that the liquid film transfer coefficient k_L is represented by three different factors in the three mechanisms:

$$k_L = \frac{D}{\delta} = 2\sqrt{\frac{D}{\pi t_e}} = \sqrt{D S} \quad \ldots\ldots\ldots\ldots \quad (62)$$

It is seen that k_L is proportional to D in the Whitman model while to $\sqrt{D}$ in the other two. Experimental evidence, however, is not very definite in this connection. Sherwood and Pigford[6], although recognising the uncertainty due to lack of precision in the values of D for liquid systems, used a value of 0.5 as the exponent of D in relation to k_L on the basis of data taken with hydrogen. Lin, Denton, Gaskill and Putnam[32] found the power on D to be 0.667 whereas for laminar flow Eucken[33] determined it to be 0.66. For turbulent flow, King[34] gave a value of 0.75, while Hammerton and Garner[35] determined values of 0.41 and 0.55 for bubbles of 0.3 cm. and 0.6 cm. diameters respectively. Rates of solution of solids in liquids, according to Danckwerts[12], point to an exponent of 0.5 for diffusivity.

The situation is a little complicated because of the lack of knowledge of the values for δ, t_e, and S as well as the inavailability of sufficient data on diffusivities and absorption rates to check these relations. It is doubtful, however, if the determination of D and k_L will simplify the problem to a very great extent as δ itself has been found to depend on diffusivity in mass transfer between solids and liquids. In such systems, where it is recognised that a true boundary layer exists, it has been found that mass transfer coefficient is proportional to the square root of diffusivity (12). That is to say, if δ is proportional to the square root of diffusivity, as is quite feasible, all the three models will lead to the same relation between k_L and D, and this line of attack to the problem will lose a good deal of its force.

Applications of the experimentally determined values of D and k_L

In spite of these limitations, determinations of D and k_L for a number of systems may be utilised in a number of ways. For instance, from the knowledge of these properties δ, t_e and S can be calculated for all these systems by substitution in the appropriate equation and compared. Although a direct measurement of δ does not seem to be an easy affair, that of t_e and S is quite possible. In fact, Danckwerts and Kennedy(12) have estimated S in their experiments for the water-carbon dioxide system by the rotating drum method and the time of contact is definitely known in absorption experiments carried out in this laboratory with a special type

of jet(36). These data should serve as additional checks on these relationships and be able to furnish some very useful information.

An attempt can also be made to visualise the thickness of surface film in absorption equipment as far as possible. When k_L and D are known, δ can be calculated with the help of equation (57) and should prove a valueable guide in the examination of various mechanisms of absorption. Variation of these properties with temperature, as well as the exponent of D which is necessary to define the relationship between D and k_L may also be utilised to interpret the dependence of δ on the various variables in the system. On the other hand, equation (44) in conjunction with the measured values of diffusivity may provide a means to calculate the average distance to which a diffusing particle will penetrate in a given time of contact. This information, coupled with the mechanical feasibility of various thicknesses, will shed some light on the problem of the magnitude of stationary of non-stationary state existent in gas-liquid absorption.

Finally, this analysis will be of value in cases where only D for a system is known. In such a case, values of k_L may be predicted for various times of contact, or for various film thicknesses, or for various rates of surface renewal by the application of an appropriate equation and the equipment most suitable for the purpose chosen.

A new diffusion coefficient

It will be useful to note, however, that throughout this

analysis differential diffusion coefficients at infinite dilution will not be employed, as they are considered inappropriate for such applications. Instead, diffusion coefficients calculated on the basis of diffusion from saturated solutions to pure liquids will be used. A little thought will show that as in practice, usually absorption takes place from a pure gas (effectively at any rate, as gas films are neglected in systems of the type under consideration) to a pure liquid, the latter way is nearer the truth and therefore preferable. In other words, it is assumed that in absorption equipment, diffusion takes place from saturated solutions to pure liquids initially, and therefore a similar diffusion coefficient will lead to a more precise representation of the relationship between the two. For this purpose, a new technique for the measurement of such diffusion coefficients is developed and will be described subsequently.

PART III

Section A

PART III

Section A

A review of the literature for the methods of determining diffusivity in liquids.

General

Diffusion in liquid systems was first observed by Parrot[37] as early as 1815. Since then numerous methods have been designed to measure diffusivity in liquids and it is only relatively recently that methods of reasonable accuracy have been developed. The presence of mass flow, lack of very accurate analytical methods, difficulty in the computation of diffusivity from rate measurements and very close control of temperature required have all been responsible for the efforts required in this direction in the course of the last hundred years. In this section the literature has been reviewed for the methods developed so far. A classification of the methods is made for the purpose as follows:

(1) Early methods.

(2) Optical methods.

(3) Electrical methods.

(4) Relative methods.

(5) Tracer methods, and

(6) Methods of estimation.

Early methods

It was Graham[38] who initiated the quantitative study of diffusion in liquids. He developed the method of layer analysis for measurements of diffusion coefficients which lent itself to a mathematical interpretation. A similar method, employed by Beilstein[39] consisted in placing a cylinder containing the solution and closed at its bottom end in a large vessel filled with the solvent up to a level slightly above the top end of the cylinder. The diffusion coefficient was calculated from the knowledge of the diameter and height of the cylinder, the initial concentration of the solution and the measurement of the final concentration of the solution after diffusion has proceeded for a known time interval.

The difficulty which arose due to mixing which occurred at the beginning of an experiment when solutions of different concentrations were brought together and the conclusion when the different portions of the solution were separated for analysis was solved by Schuhmeister[40]. He introduced a shearing mechanism for forming a sharp boundary initially and for removing samples for analysis with minimum of mixing. His method consisted in sliding an inverted cylinder, containing the solvent and fixed on a frame, over another lower cylinder containing the solution to start the diffusion. At the end of the experiment, the upper cylinder was slid back and the contents of the two analysed.

A modification used by von Wogan[41] consisted of

eight glass plates with a two centimetre hole in the centre of each instead of the cylinders. These plates fitted into a frame and when the holes were lined up formed a diffusion column the layers of which could be removed at will and analysed. Oholm[42] used this apparatus in his later work but had only four plates of brass which were carefully ground so that Stefan's tables[43] could be utilised. This gave more consistent results per layer than the older methods. The results obtained by these methods, however, cannot be interpreted to lead to either integral or differential diffusion coefficients, as has been pointed out by Hartley and Runnicles[44], if the variation of diffusivity with concentration is large. The same is true for other works in which Stefan's tables are used.

Fick[45] carried out diffusion measurements by immersing a series of cylindrical tubes to half their length in a saturated salt solution. The upper half was then filled with water and the concentration distribution within the tubes at various time intervals was determined with an hydrometer. Griffin[46] improved this apparatus by placing several tubes through a partition which divided the upper and the lower halves of a box-like container. The partition served to separate the solution from the solvent except inside the tubes where diffusion took place. The method has the disadvantage of interference with the process of diffusion.

Quite a useful way of forming a sharp boundary between a

solution and a solvent initially is to allow the denser solution to flow under the lighter one. Scheffer[47] improved this method of Graham by using a pipet with a stopcock at the top to facilitate introduction and withdrawal of solutions with less mixing. Arrehenius[48] modified this apparatus still further by introducing a mercury layer at the bottom of the apparatus to assure a flat surface and a cork was used for the insertion of the pipet. Experimental conditions were made suitable for the use of Stefan - Kawalki[43] tables. Svedberg[49] found this method to lead to results comparable with those obtained ultramicroscopically.

Some of the difficulties inherent in free and restricted diffusion measurements were avoided by Clack[50] who employed a steady-state method which was developed by him to a high degree of accuracy. The vessel containing the solution was immersed in a larger container of solvent and then suspended from the arm of a balance. The loss of weight of the solution vessel with time was recorded. The establishment of the steady state was inferred from the uniform loss of weight and the integral diffusion coefficient computed from the value of this loss, the density of the solution, and the cross section of the diffusion vessel. In his later experiments, he reduced the time required for the establishment of a steady state by using a battery of short tubes of small diameter without sacrificing the sensitivity of the method - a step towards the recent diaphragm cell method.

Optical methods

Optical methods for the determination of diffusivity are by far the most numerous and have the advantage of following the rate of diffusion without causing any disturbance in the system. As early as 1800, Wollaston[51] showed the possibility of a relationship between the refraction of light and the concentration of different layers in a column of liquid and this relationship was formulated mathematically by Wild and Simmler[52]. Gouy[53] has also described the propagation of light waves through a column containing a solution whose concentration vary with height which is fundamental to all the optical methods for the determination of diffusivity.

Wiener[54] was the first to use an optical method for the experimental determination of diffusivity. Light of a definite wavelength was allowed to pass through the diffusion column and the interference bands were recorded photographically. As the diffusion proceeded, the centre of the band was deflected and the displacement was measured by means of a cathetometer. From the relation derived for the concentration and the displacement of the interference band, the diffusivity was calculated.

Wiedeberg[55], Ulmann[14], and Tiselius[56] followed diffusion by measuring the absorption of light by the diffusing solution. The last measured the concentration of proteins in a diffusion column by photographing the solution using light of a wavelength absorbed by the protein but not by the solvent.

The extent of blackening of the photographic plate showed the extent to which diffusion had proceeded.

Several optical methods were investigated by Thovert[57] including one in which he obtained the gradient curve traced directly in rectangular co-ordinates with the aid of a cylindrical lens. He modified Wiener's apparatus by using a better source of light with collimator and by measuring the maximum displacement of the interference band with time with the aid of a micrometer ocular. His curves compare favourably with those obtained by more recent optical methods.

Heimbrodt[58] improved Wiener's method by sharpening the distorted image of the slit by employing a narrower slit placed against the diffusion cell at an angle of 45°.

Change in the intensity of colour of the diffusing solution and the formation of precipitates in gels was utilised by Bechhold and Ziegler[59] to follow the progress of diffusion.

Clack[50] employed a diffusion channel of rectangular cross-section and followed the progress of diffusion by an optical arrangement similar to that of Thovert[57]. By this apparatus he was able to measure the refractive index gradient at different levels in the column and hence the differential diffusion coefficient as a function of concentration. His work thus lead to the differentiation between integral and differential diffusion coefficients as also to the elimination of some of the defects of optical systems when applied to free diffusion as the change in refractive index with height in the steady state is much slower.

Svedberg[49] developed a very ingenious method for the measurement of diffusion of proteins by utilising the fact that when two solutions of different concentrations are placed in contact without mixing, a sharp boundary is present between them initially which is increasingly blurred with time due to diffusion. This can be determined quantitatively in many cases.

A microscopic method was applied by Westgren[60] who investigated the diffusion of gold and selenium sols. His cell consisted of a microscopic slide and a cover glass. The sol was thrown to the bottom of the cell by centrifugal force, the apparatus was then placed under the ultramicroscope and the diffusion was followed by counting the number of particles at different heights over suitable time intervals.

The "blurring of the boundary" method was applied to dyes by Furth[27] who used a colorimetric standard to follow the progress of diffusion. The cell, having a partition to separate initially the solvent from the solution together with the comparator chamber was placed in the field of a microscope and diffusion was started by removing the partition rapidly by means of an electromagnet. With the help of a narrow slit, the microscope could be focussed on a layer of solution whose concentration was the same as that of the reference liquid and from the height of such a layer and time, the diffusion coefficient was calculated. A microdiffusionmeter has been described by him in a recent paper.

Lamm[61] employed a scale method which had previously been used by Littlewood[62]. His method consisted in photographing

a transparent scale through the diffusion column, the distortion of the transparent scale giving the extent of diffusion. Later he used a slit method in which the height of the diffusion cell, the concentration at which will let a beam of light pass through two fixed slits was utilised.

Zuber[63] has used a micro-method in which the total reflection of light by a layer of solution of definite composition and therefore of definite refractive index is utilised to follow the progress of diffusion of colourless solutions (just as a colormetric standard is utilised in Furth's method). Dean[96] later modified this apparatus and recorded the results photographically.

An interference method coupled with a very sharp boundary between the solution and solvent initially was employed by Philpot[64].

Interferometric concentration determinations have also been used by Rogener[65] and by Calvet and Chevalerias[15]. A twin diffusion cell was employed. The double-slit of the interferometer was perpendicular to the (direction of) concentration gradient in the former's experiments while it was parallel to it in the latter's. The former obtained two sets of interference fringes, that produced by the uniform solution in the comparison cell serving as the reference mark. The diffusion cell could be displaced vertically by means of a micrometer screw. The diffusion coefficient was calculated from the known value of the distance between the slits and the displacement of the interference fringes (i.e.

the change in concentration) with height.

In Calvet's experiments, a system of interference patterns was obtained representing for every value of the height of the diffusion cell the difference in refractive index with the liquid in the comparison cell. A part of these patterns, corresponding to a narrow vertical slit was photographed on a continuously rotating drum giving the relation between time and concentration.

A quantitative theory of the interference method suitable for the evaluation of diffusivity was given by Kegeles and Gosting[66] which was tested experimentally by Longsworth[67]. The latter found his results to agree with the theory with an average deviation of 0.15% only. The theory was further tested and improved by Gosting and Morris[66]. By the same method, Gosting later obtained results on aques potassium chloride diffusion which agreed within 0.1% with those obtained by Harned and associates with conductivity method[68].

Kraus and Tye [69] have described an apparatus in which the cell itself acts as a cylindrical lens. It is capable of giving diffusion coefficients of liquids with an accuracy of a few per cent, but at low concentrations the apparatus is not very sensitive because of small changes in the refractive index of the system.

English and Dole[70] have measured the diffusion coefficient of sucrose in highly concentrated and supersaturated solutions by both the Schlieren[71] and the Gouy[66] [67] [72] methods and found the latter to be more accurate.

Electrical methods

Electrical methods have been employed for a measurement of concentration along a diffusion column in systems containing electrolytes in solution. Weber[73] arranged a cell in such a way that the potential difference between a metal and its ions in different layers of a diffusion column could be measured. He also measured the conductivity between two boundary layers as the material diffused. Niemoller[74] measured the change in conductance through a capillary tube containing the solution of a diffusing electrolyte.

Electrical conductivity between pairs of electrodes spaced at intervals along a diffusion column was measured by Haskell[75]. Since the diffusivity of electrolytes generally increases with dilution, it was contended that ions move faster than undissociated molecules and the frictional resistance encountered by the former is lower.

A conductance method for the determination of differential diffusion coefficients of electrolytes was developed by Harned and French[68] which was later improved by the former and his associates to a very high degree of accuracy. A Tiselius type of cell of lucite consisting of two symmetrical parts, one sliding over the other, was used and values of diffusion coefficient of a number of electrolytes at various concentrations were determined. The results obtained were the first of sufficient accuracy in very dilute solutions and those obtained for the diffusion of potassium chloride in water have been found satisfactory for the calibration of a diaphragm diffusion cell.

Relative methods

Northrup and Anson[76] have devised an apparatus for diffusion measurements which has the advantages of speed and simplicity. It consists of two chambers separated by a horizontal porous diaphragm of glass. One of the chambers contains the solvent while the other contains solution. By maintaining the solutions in the chambers uniform in concentration by some sort of stirring (density or otherwise) the process of diffusion is confined to the pores of the diaphragm. A high concentration gradient may be maintained thereby reducing the time of experiment and the process may be treated as a steady state one if the volumes of the two chambers are sufficiently large compared to the volume of the pores of the diaphragm. The porous diaphragm helps to reduce error due to convection and vibration. Since the effective size of the pores is not known, the apparatus has to be calibrated with a substance of known diffusion coefficient and hence the method has the limitation of being a relative one.

The porous diaphragm method was further improved by McBain and his associates[77] who showed that the results obtained by this method were reproducible to within a few tenths of a percent and were independent of the nature and porosity of the diaphragm.

Hartley and Runnicles[44] studied the variation of mean diffusivity of potassium chloride solutions with concentration employing a tilted diaphragm cell which had glass spheres of appropriate densities to touch the diaphragm surface in both

the chambers. The cell was rotated to stir the solution and concentrations were determined conductometrically.

The problem of calibrating a diaphragm cell and the variation of diffusion coefficient with concentration has been discussed by Gordon[24].

If filter paper is used instead of a sintered glass in the diaphragm diffusion cell, the time required for an experiment is considerably reduced and the method is suitable for systems requiring quick determinations. Gage[78] has used such a cell and found the standard error of the mean of six experiments to be about 1.5 per cent.

The diaphragm cell technique has been improved considerably by Stokes[23] who showed the limitations of the "density stirring" which make mechanical stirring essential for diffusion measurements by this method. He employed magnetically operated stirrers in his cell, the speed of which was also shown to affect the results. He discussed the problem of calibration of such a cell and compared his results for potassium chloride solutions with those of Harned and his associates[68] showing very good agreement. At higher dilution than .05N of potassium chloride, however, his results were higher. This was ascribed to surface transport effect on the pores of the diaphragm as shown by Mysels and McBain[79]. Later, the technique was applied to a number of systems by him and his associates and the results obtained were compared with those obtained by the Gony method showing substantial agreement.

Smith and Sterrow[20] redetermined the optimum rate of stirring and the time required for the attainment of equilibrium, i.e., the steady state in the diaphragm before actual measurements should begin in that method.

Tracer methods

Robinson and Drew[80] have employed radioactive isotopes for diffusion measurements and found that the technique gave better results than any of the previous analytical methods. It was assumed that the radioactive isotopes behaved in the same way as the non-radioactive ones in spite of a slight difference in mass. With this technique, it was possible to work with solutions of 10^{-5} M concentration without much difficulty.

Measurements of self-diffusion of water by using deuterium as the tracer were made by Orr and Butler[81], by Anderson and Saddington[82], by Wang[83] and by Graupner and Winter[84]. The last two employed a diaphragm cell and used ^{18}O as tracer as well to verify the results. Wang also employed the tracer liquid in a narrow capillary to verify his diaphragm cell results and concluded that the rate of stirring in the diaphragm cell does affect the measured diffusion coefficient.

Isotopic labelling of an ion in a diaphragm cell was also used by Nielsen, Adamson and Cobble[85] who confirmed the findings of Stokes[23] as to the surface transport phenomenon at high dilutions in such a cell.

Methods of estimation

Arnold[86] has applied the kinetic theory of gases to diffusion in liquid systems. He derived an empirical relation for the estimation of diffusivity in liquids:

$$D = \frac{B\sqrt{\frac{1}{M_1} + \frac{1}{M_2}}}{A_1 A_2 \; Z_2^{1/2} S^2}$$

where A_1, A_2 and B are constants; M_1 and M_2 are the weights of the substances involved; Z_2 is the viscosity of the solvent in centipoises at 20°C and S is the sum of the cube roots of the molecular volumes of the solute and the solvent. The equation has been applied to calculate diffusion coefficients of many systems for which data are not available and has been found useful in many cases. Trevoy and Drickamer[87] found their experimental results to agree with those given by the Arnold equation.

On the basis of relations suggested by the Eyring theory of absolute reaction rates[19] and the Stokes - Einstein equation (Part II), Wilke[88] has developed a method for the estimation of diffusion coefficients in liquids through the group $F = \frac{T}{D\eta}$ where T is the absolute temperature, η is the viscosity of the solvent and D is the diffusion coefficient, which is considered independent of temperature for a given solute-solvent system. For the diffusion of various solutes in a given solvent, F was treated as a function of the molal volume of the solute. Observed data for the diffusion of

various substances in water, methyl alcohol, benzene and fourteen other solvents were compared with the calculated values and an average deviation of ten per cent was found.

Another method for the estimation of diffusion coefficient in liquids was developed by Othmer and Thaker[89]. Their relations are:

$$D_w \times 10^5 = \frac{14.0}{\mu_w^{1.1} V_m^{0.6}} \quad \text{for diffusion in water.}$$

$$\text{and } D \times 10^5 = \frac{14.0}{\mu (1.1 L_s / L_w) V_m^{0.6} \mu_s^{\delta}} \quad \text{for diffusion in other solvents}$$

where μ is the viscosity, L is the latent heat of vaporisation and Vm is the molecular volume of the solute. The correlation is based on experimental data from widely varying sources, and some assumptions. A nomograph is given which is useful with dilute solutions.

Resúme

Although it is more than one hundred years since experimental work for the determination of diffusivity in liquids was started, elaborate methods of sufficient precision have been developed only relatively recently. Out of the continuous efforts of numerous workers have emerged three distinct methods - the conductivity method, the diaphragm cell method and the so called Gouy method - the accuracy of which, if applied to a proper system, leave little to be desired. The development of the conductivity method to its present state of precision is due to Harned and his associates

and is applicable to the diffusion of electrolytes at low concentrations. The diaphragm cell method, on the other hand, can be used for both electrolytes and non-electrolytes, but not at too low concentrations of the diffusing substance because of the surface transport phenomenon. Relatively large concentration gradients may be employed and analysis may be carried out in situ or otherwise depending on the method available. The method has the disadvantage of being a relative one, nevertheless, it is the simplest and for certain systems the best method. Usually the method gives integral diffusionm coefficients from which differential values may be calculated by the methods discussed in Part II if required. Differential coefficients can also be obtained directly by this method if sufficiently sensitive method of analysis in situ is available e.g. conductometric analysis in the case of an electrolyte. The Gouy method is the most recent of them all and was developed by Longsworth, Keegles, and Gosting in the United States and by Coulson, Cox, Ogston and Philpot in Britain. It is probably the most accurate and convenient method for determining diffusion coefficients in solutions of moderate and high concentrations. It has the advantage of being an absolute method whose intrinsic accuracy has been claimed to be higher than other methods. The technique is particularly suitable for substances of high molecular weights, but concentration difference across the boundary should be considerably reduced if the differential diffusion coefficient of a substance having concentration-dependent diffusion coefficient is being measured.

An estimate of the diffusion coefficient can be made from the relations of Arnold, Wilke and of Othmer and Thaker. The equations of Eyring and of Stokes - Einstein may also be employed if the data required are available. None of these relations have been tested adequately.

PART III

Section B

PART III

Section B

Preliminary Experiments

In the last part, it has been said that the experimental evaluation of diffusivity and liquid film transfer coefficients should prove a valuable means for the understanding of the mechanism of gas absorption. Although data for liquid film transfer coefficients are not very numerous in the literature, those for diffusivity are still scarcer, the reason being, as Bakowski[90] rightly remarked: "the experimental procedure for determining this property (i.e. diffusivity) is probably more laborious than a direct determination of the mass transfer coefficient itself." One of the main purposes of this work, therefore, has been to determine the diffusivity of a few gases in different liquids and to examine its implications on the basis of various assumptions made as to the mechanism of gas absorption with special reference to the data for liquid film transfer coefficients of the same systems.

In the first place, the problem resolved itself into two parts, viz.,

(1) Design of suitable apparatus for diffusion keeping in mind the gaseous nature of the solute and consequently its tendency to escape from solution. In the case of slightly

soluble gases, the volumes of fluids had to be large enough to permit of accurate analysis.

(2) Choice of sufficiently accurate method of analysis to determine the extent to which diffusion has taken place either continuously or after a diffusion run of a certain duration.

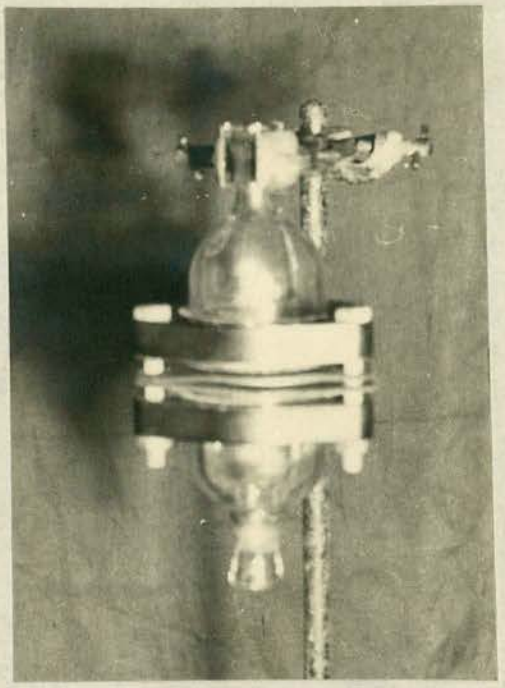
The apparatus

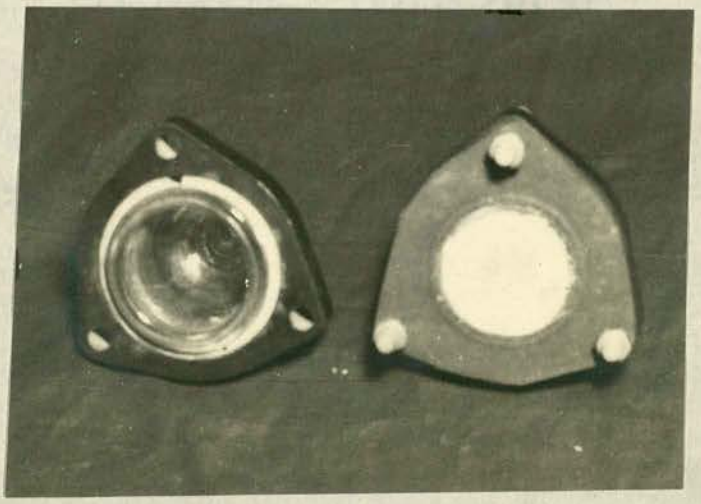
To start with a few experiments were carried out on diffusion of potassium permanganate solution in water to indicate the suitability of the apparatus qualitatively. It was hoped that some form of apparatus would be used in which the dimensions of the diffusion-channel would be definitely known. A very simple cell was constructed which consisted of two compartments of equal volumes joined by means of a narrow capillary of known diameter and length. With very narrow capillaries, diffusion was found to be too slow while wider ones tended to induce mass flow. A number of capillaries of narrow bore were then substituted but the rate of diffusion was considered still inadequate in view of the systems to be investigated. The idea of employment of diffusion channel of known dimensions had to be abandoned for the time being and the possibility of using any of the existing methods for the determination of diffusion coefficient of gas-liquid systems with necessary modifications was examined.

Of the three modern methods of sufficient precision, viz., the conductivity method, the Gony method and the diaphragm cell method reported in the literature, the last one seemed to offer the following advantages for the determination of diffusivity of gases in liquids.

1) Comparatively large volume of solutions available for analysis.
2) Provision of adequate area for diffusion giving sufficient concentration changes in the solutions in the two cell compartments after a diffusion run of reasonable duration.
3) Availability of adequate relations for the computation of diffusivity from such concentration changes.
4) Simplicity and ease of its construction and operation.
5) Accuracy of the method as proved by results obtained by various workers being comparable with those obtained by other methods.
6) Comparative freedom from mass flow or streaming due to minimising of the effect of vibration, convection and density gradients (heavier solution put in the lower compartment).
7) Availability of suitable standard substance with established value of diffusion coefficient for calibration, and
8) Being a closed system, the volatility of the diffusing substance offered no limitation.

A modification of Stokes' apparatus[23] was employed and advantages of using metallic porous plate was investigated.





PHOTOGRAPH OF THE DIFFUSION CELL WITH METAL SINTER

For this purpose, a diffusion cell consisting of two compartments of glass pressed ends bolted together with bakelite flanges and the bronze porous plate at the centre was constructed. A photograph of this cell is given. Diffusion runs were carried out with water and potassium chloride for calibration but were unsuccessful because of the turbidity caused by the metal plate. Acids could not be employed to clean the metal sinter. Neoprene washers were also attacked in test runs of organic liquids and work with metal sinters had to be discontinued. An all glass cell with glass sinters and B 14 standard joints was then designed which yielded satisfactory results. A detailed account of this cell together with the method of procedure will be given later.

Method of Analysis

Three methods were available for estimating the amount of gas dissolved in liquid, viz.,

(1) Volumetric.

(2) Analytical, and

(3) Optical.

Aikman[91] has described a method for the measurement of solubility of gases in liquids which consists in boiling the dissolved gas off and measuring that evolved by means of a gas burette. A similar method was tried first but was found incapable of yielding sufficiently accurate results because of the low solubility of the gases concerned which

became more critical with solutions far from saturated as obtained at the end of a diffusion run. The reverse process of saturating the liquid containing the dissolved gas and measuring the amount of gas required for the purpose also failed and recourse was taken to a method for measuring the vapour pressure of unsaturated liquid. It consisted of introducing the unsaturated liquid into a bulb which had been in connection with another containing the pure liquid and which had been evacuated until the pure liquid boiled, the vapour space above the latter being then disconnected with the bulb by means of a stop cock. The unsaturated liquid released its gas on entry into the bulb because of a sudden fall in pressure and the difference of vapour pressures of the two liquids was recorded by means of a leg of the pure liquid. Although the method seems to offer no difficulty theoretically, the vapour pressure of the unsaturated liquid could not be measured accurately enough, especially in the case of high-boiling liquids. Volumetric methods having thus been found unsuitable, the analytical methods were tried. These remarks, however, apply only when both the compartments of the diffusion cell are filled with liquid, i.e., when diffusion takes place from solution into pure solvent and the solute is not present in any of the compartments in the gaseous state.

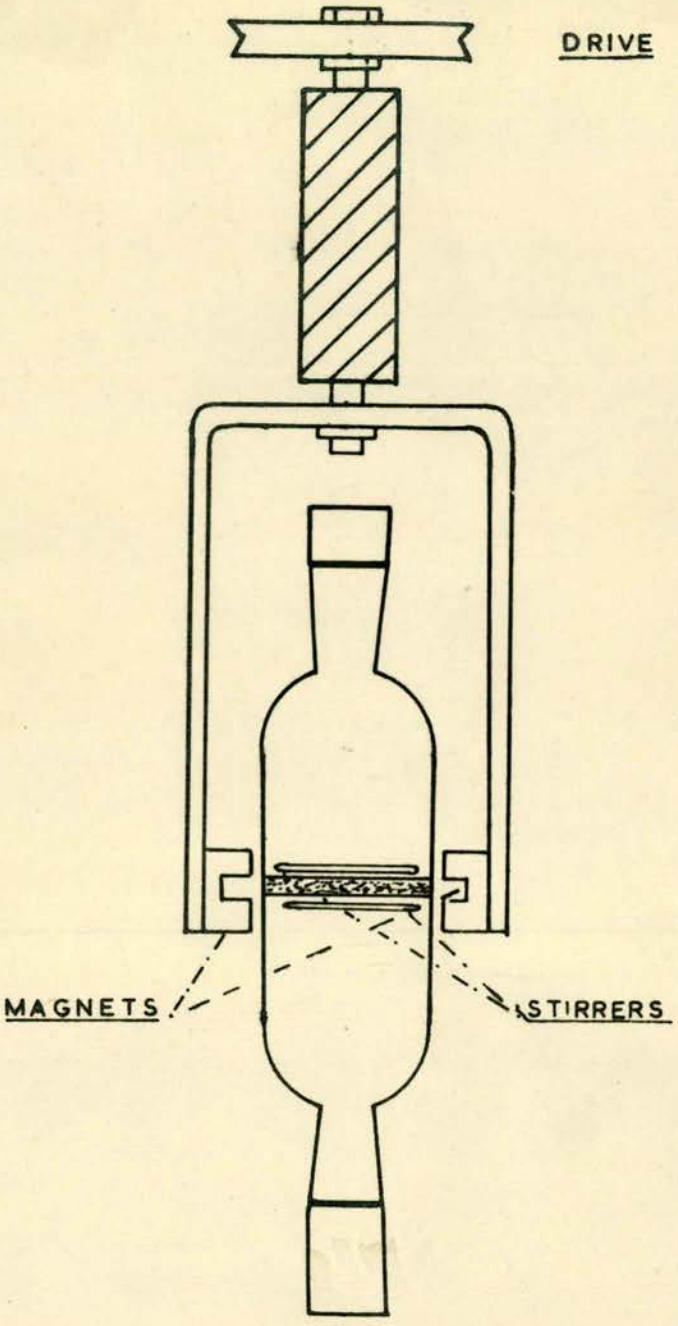
Of the four gases used in these experiments, viz., hydrogen, ethylene, carbon dioxide and sulphur dioxide, the last two can be easily analysed but the first two offered difficulty because of small volumes of gas contained in the

dilute solution obtained at the end of a diffusion run. Analytical methods, therefore, were kept in reserve pending failure to find some other suitable method applicable to all the systems.

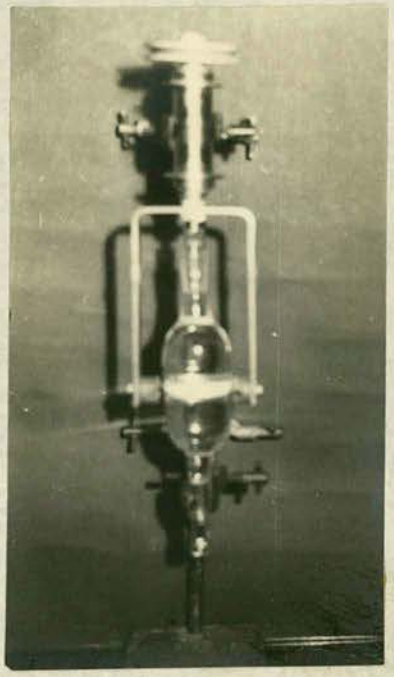
Coming to the optical methods, measurement of change in refractive index of a liquid due to the presence of varying amount of dissolved gases suggested itself first and it was enquired if a method was available by which such differences of refractive indices could be measured with sufficient accuracy. Ordinary refractometers, such as the Abbey were obviously not good enough to measure such small changes and a preliminary examination showed that an instrument about one hundred times as sensitive as the Abbe will be just good enough. Both Rayleigh and Zeiss interferometers were acquired of which the latter was found to be more satisfactory because of its compactness, ease of manipulation and easier temperature control. Experiments were carried out with solutions of different concentrations and the interferometric readings noted. A plot of interferometric reading against concentration served as a ready reference for reading off concentrations of the gas in liquid if the corresponding interferometer reading were taken. The method was found quite convenient and used in the first series of experiments.

The apparatus to be used and the method of analysis for the system being thus decided, experiments were carried out to measure diffusivity of ethylene and hydrogen in dekalin and toluene. A detailed description of the apparatus and the method of procedure is given in the next section.

PART IV



DIFFUSION CELL.



PHOTOGRAPH OF THE

DIFFUSION CELL

PART IV

Experimental and Results

The diffusion cell

As shown in the diagram, it consists of a cylindrical cell made of pyrex glass which is divided into two compartments by means of a circular glass porous disc. The ends of the cell narrow down to B.14 sockets to which B.14 stoppers can be fitted. The porous discs were supplied by J.A. Jobling and Co. Ltd., and discs of three grades of porosity, namely 1, 2 and 3 of pore diameter range 100-120, 40-50 and 20-30 microns respectively were tried in trial experiments. These showed the inadequacy of the first two grades for diffusion experiments because of their incapability to check mass flow and the last grade of sinters only, therefore, were employed throughout in these experiments. Table I gives further details of the cells employed.

TABLE I

The diffusion cells.

Cell No.	Sinter			Volume of the upper chamber ml.	Volume of the lower chamber ml.
	Thickness mm.	Diameter cm.	Pore diameter microns		
1	3	4.5	20 - 30	71.5	77.6
2	3	4.6	20 - 30	60.6	63.7
3	3	4.5	20 - 30	62.0	62.8
4.	3	4.6	20 - 30	53.3	59.8

The stirrers

Each compartment was provided with a stirrer to keep the solutions uniform in concentration. These were made of a length of glass tubing of about 7 mm. diameter and length slightly less than the cell diameter, into which were sealed a number of soft iron wires. The number of wires sealed was adjusted so that the stirrer in the upper chamber sank while that in the lower floated. The stirrers were actuated by means of two permanent magnets coated with acrylate resin to prevent corrosion under thermostat water. The magnets were attached to the ends of a brass strip bent in the shape of an inverted U as shown in the figure. The height of the cell was adjusted in such a way that the magnets were just opposite the sinter. The brass strip with the magnets was rotated round the cell by means of a pulley attached to its top so that each side of the sinter was wiped twice per revolution of the strip. In the beginning, a variable speed motor was used to drive the pulley, but very inconsistent results were obtained due to large variation in its speed in course of a diffusion run - the lower speeds being insufficient to keep the solutions uniform in composition while higher speeds tending to promote mass flow. A constant speed motor was then substituted and a speed of 60 R.P.M. was found to give best results after trial, as has been the case with Stokes'[23], Smith and Storrow's[20], and Nielsen et al.'s[85] experiments. Stokes has already shown that this speed is sufficient to maintain the solutions uniform in composition in the two compartments.

The thermostat

It consisted of a copper tank, 18" x 12" x 12", the sides of which were insulated with cardboard. It was provided with a stirrer and a 500 watts heater which was controlled by an ordinary toluene-regulator (filled with chloroform) and Sun-Vic relay. Beckmann thermometer showed its temperature to be maintained within ± .02°C of that required which was considered sufficiently accurate for its purpose.

Materials used

Potassium Chloride:- Analar grade as supplied by British Drug Houses Ltd. Dried and used without further purification.

Dekalin:- Supplied by Hopkins and Williams Ltd. Redistilled and only fraction between 185 - 186°C at atmospheric pressure used. $D_{20°C}$ = 1.4739.

Toluene:- Supplied by J.F. Macfarlen and Co. Ltd. Redistilled and only fraction between 110° - 111°C at atmospheric pressure used. $D_{20°C}$ = 1.4958.

Water:- Pure freshly distilled water degassed.

$D_{20°C}$ = 1.3330.

Hydrogen, Ethylene and Carbon dioxide: as supplied by the British Oxygen Co. Ltd., direct from cylinders.

Sulphur dioxide:- As supplied by A. Boake, Roberts and Co. Ltd. direct from the syphon.

Determination of cell constants

As the effective pore size of the sinter is not known, the cell constants were determined by carrying out diffusion

of a decinormal solution of potassium chloride into water at 25°C as is the established practice. The value for the diffusion of a decinormal solution of KCl into water until about 25 per cent of the chloride has diffused into the other compartment given by Stokes[23], viz., 1.667×10^{-5} $cm^2/sec.$ on the basis of his own and of Harned and associates' experiments [82] was accepted and used in the calculation of cell constants. All liquids used in this investigation were degassed prior to employment to avoid bubble formation in the sinter itself or in any of the cell compartments as described. The liquid was heated to boiling in a litre flask with standard B24 opening and immediately stoppered thereafter with a B24 stopper (which had been ground previously to fit closely without the use of any lubricant) and allowed to cool to the experimental temperature in a thermostat. It was taken out of the flask only just before use.

The cell was cleaned, dried and then the lower chamber was filled with degassed .1N. solution of potassium chloride which was allowed to drain through the sinter in order to displace air from the pores. The proper stirrer was then put into the compartment which was refilled with the solution at the thermostat temperature and quickly stoppered avoiding any air bubble inside. The upper chamber was then filled with degassed distilled water after being washed with the same twice and stoppered after the stirrer had been put into it. The cell was then put on its seat in the thermostat and its position

adjusted so that the sinter was horizontal and the stirrers did not touch the sinter surface. This was important as the contact of stirrers with the sinter was found to cause the latter to wear as well as to lead to inconsistent results. Magnets of the shape used were particularly useful to keep the two stirrers away from the sinter surface if the height of the cell was properly adjusted with respect to the magnets. This being done, the stirrer-motor was started and the time noted. After a preliminary period of four hours, which was found to give best results and was found sufficient by others, the stirrers were stopped, the upper chamber containing the less concentrated solution was drained, washed with distilled water and refilled with distilled water at thermostat temperature. After the stirrer had been put in, the cell was stoppered and put back on its seat properly and the magnets driven. This was taken as the start of the diffusion run which was carried on until about 25 per cent of the contents of the lower chamber had diffused into the upper. The run was then stopped, the contents of the two chambers were taken out carefully as to avoid mixing and analysed. A decinormal solution of silver nitrate was used to determine the chloride content of the solutions with fluorescein as indicator(95). A material balance at the end of a run showed absence of leaking due to non-application of a lubricant to the stoppers. Difference in the densities of the two solutions was utilised as a means of elimination of mass flow by putting the pure liquid in the upper compartment

as shown desirable by Stokes[23], instead of using it for the so called "density stirring". All the analyses were carried out in duplicate and the mean value of each pair is given. The whole operation of filling the cell with liquids, putting it properly on its seat and starting the magnets does not take more than a minute and should not matter for a run lasting more than twenty four hours. From the change of concentration in the two compartments measured and the time required to bring about this change together with the knowledge of the volume of the two compartments, the cell constants are calculated by substitution in equation (27). Following is a sample calculation of cell constant from measurement of concentration changes in the two cell compartments.

Temperature of the experiment: 25°C.

Cell: No. 4.

Volume of upper chamber: 53.3 ml.

Volume of lower chamber: 59.8 ml.

Initial concentration of KCl in the solution in the upper chamber = 0.

Initial concentration of Potassium chloride in the solution in the lower chamber = .1003N.

Time of equilibrium allowed = 4 hours.

Duration of the diffusion run = 95 hours.

Final concentration of Potassium chloride in the solution in the upper chamber = .0242N. (=6.05 ml .1NA_gNO_3).

Final concentration of Potassium chloride in the solution in the lower chamber = .0786N. (=19.65ml .1NA_gNO_3).

Diffusion coefficient of .1NKCl in water at $25^{\circ}C$

$= 1.667 \times 10^{-5} cm^2/sec.$

From equation 27,

$$\text{cell constant } K = \frac{1}{t \times D} \log_e \frac{C_{f1} + C_{f2} \times \frac{V2}{V1}}{C_{f1} - C_{f2}}$$

$$= \frac{1}{95 \times 3600 \times 1.667 \times 10^{-5}} \log_e \frac{.0786 + .0242 \times \frac{53.3}{59.8}}{.0786 - .0242}$$

$$= \frac{1 \times 10^5}{95 \times 3600 \times 1.667} \log_e 1.841$$

$= .107/cm^2.$

Similarly, other determinations of the cell constant were made and table II contains further information about the same.

TABLE II/

TABLE II.

Determination of the cell constant.

Reference System = .1N. Potassium Chloride Solution - Water.

Temperature. 25°C. Time of equilibrium. 4 hours.

D_{KCl} at 25°C. 1.667×10^{-5} cm^2/sec.

$$K = \frac{1}{D_{KCl} \times t} \log_e \frac{C_{f1} + C_{f2} \times \frac{V_2}{V_1}}{C_{f1} - C_{f2}}.$$

Cell Number	Time (hours)	Initial conc. in lower chamber N	Initial conc. in upper chamber N	Final conc. in lower chamber NC_{f1}	Final conc. in upper chamber NC_{f2}	Cell constant K/cm^2	Mean K cm^{-2}
1	43.0	0.1N. Approx.	Nil	0.07717	0.02149	0.192	
1	45.0	0.1N. "	Nil	0.07604	0.02223	0.193	
1	43.5	0.1N. "	Nil	0.07759	0.02168	0.195	0.194
1	43.0	0.1N. "	Nil	0.07759	0.02206	0.197	
1	43.25	0.1N. "	Nil	0.07759	0.02168	0.193	
2	42.5	0.1N. "	Nil	0.07586	0.02242	0.206	
2	43.0	0.1N. "	Nil	0.07511	0.02242	0.211	
2	43.0	0.1N. "	Nil	0.07548	0.02186	0.206	0.206
2	44.0	0.1N. "	Nil	0.07511	0.02242	0.206	
2	44.0	0.1N. "	Nil	0.07567	0.02205	0.201	
3	43.0	0.1N. "	Nil	0.07455	0.02492	0.241	0.242
3	41.0	0.1N. "	Nil	0.07397	0.02376	0.243	0.108
3	43.0	0.1N. "	Nil	0.07212	0.02466	0.246	
3	43.25	0.1N. "	Nil	0.07322	0.02472	0.238	
4	95.0	0.1N. "	Nil	0.07860	0.02420	0.107	
4	95.0	0.1N. "	Nil	0.07800	0.02460	0.110	0.108
4	95.0	0.1N. "	Nil	0.07880	0.02400	0.106	

Determination of the diffusion coefficients of gases in liquids

The procedure for the determination of diffusivity of gases in liquids is necessarily the same as the determination of the cell constant except only that the pure liquid is put in the lower chamber. The time of equilibrium allowed is again four hours but the total time of a diffusion run was varied and was not necessarily of the order to allow 25 per cent of the diffusing substance in solution to diffuse into the upper chamber. This variation in the duration of a diffusion run as well as the variation of the initial concentration of the solution in the upper chamber enabled one to follow variation of diffusivity with concentration to a certain extent. The method of analysis of the solutions obtained at the end of a diffusion run, however, was different. Measurement of changes in refractive index of solutions due to varying amount of its gas content was utilised. The Zeiss interferometer was employed in the course of this investigation, a description and the way of operation of which is described by Adams[92]. A brief account of the manipulation with necessary modifications from the reference will be given.

Measurement of gas-concentration in liquids by the Zeiss interferometer.

There are three factors in the Zeiss interferometer which are to be controlled closely to obtain satisfactory results, viz., the scale, the matching of the interference bands, and the temperature control of the water-chamber.

The scale consists of a circular scale and a vertical one,

the displacement of which is proportional to the change in the angle of the prism through which the light from the solution to be examined passes. Before using the zero reading has to be always checked and back lash error avoided which otherwise is a very serious source of error.

The matching of the interference bands is a bit difficult and requires a good deal of experience. This has to be done after both the sets of interference pattern show no curvature and the oncoming bands are always to be brought from the same direction. It is preferable to count the oncoming bands from the left past the central one of the reference pattern and use a particular one as the central one, say the fourth. It is not very infrequent to miss the right band which corresponds to fifteen divisions on the circular scale, but repeating the process four or five times helps to eliminate this error. All the lenses should be kept clean and freed from moisture deposits which is a source of serious trouble.

The temperature control of the water chamber is very important and it is advisable to keep it constant by adding hot or cold water and checking with a thermometer. The water chamber is provided with a stirrer the use of which makes the temperature uniform and the bands straighten quickly if the water is stirred after the cell with the liquid to be examined is put into it. Difference in temperature affects the reading of the scale, which may be significant, especially if the liquids with low concentrations are examined.

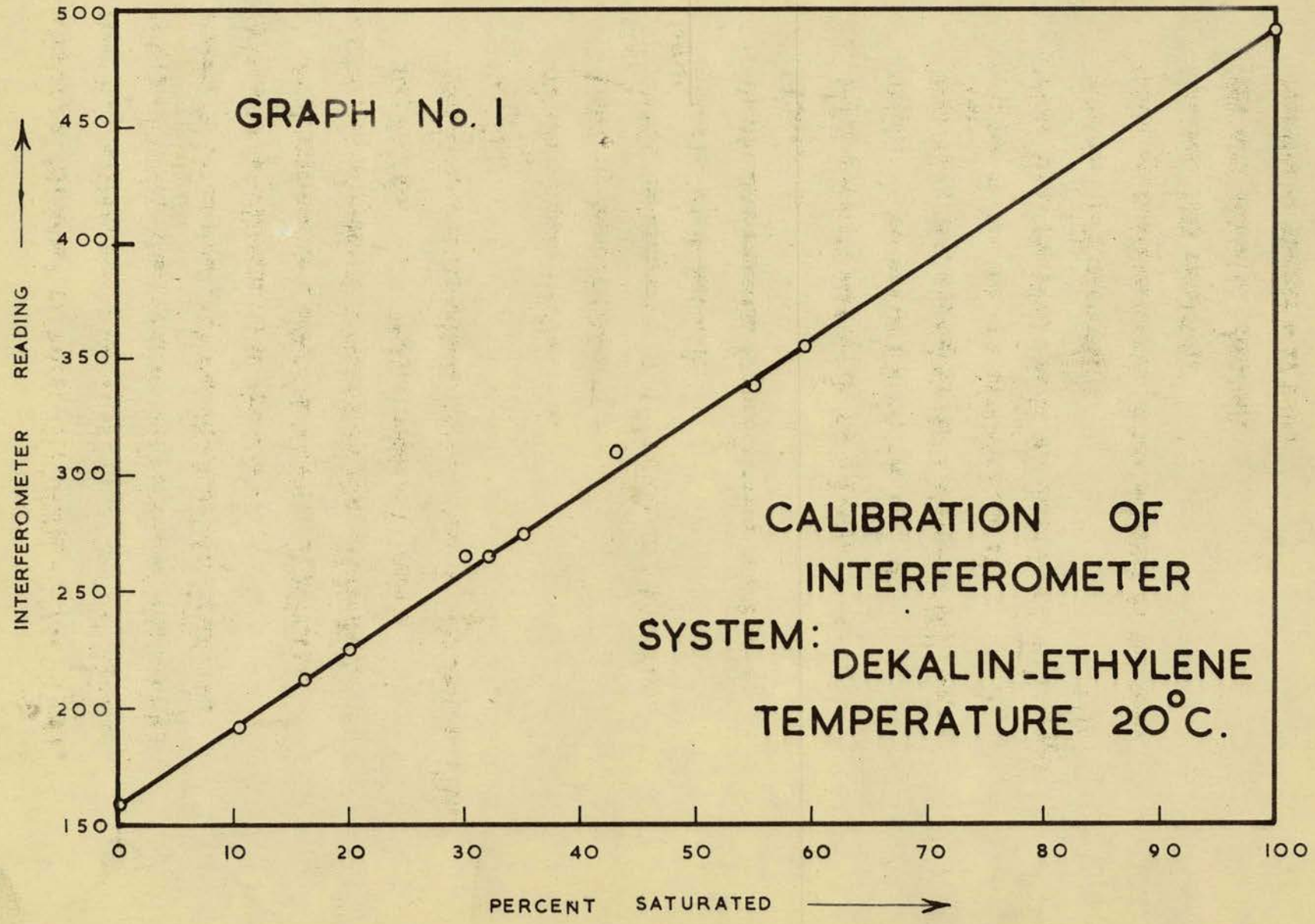
For calibration purposes, a saturated solution of the gas in liquid was first prepared. It consisted in evacuating the flask containing the liquid repeatedly and then filling with the gas until almost all of the air inside it was replaced by the gas. It was then well shaken and was allowed to stand with occasional shakes in a thermostat at the temperature desired. The flask was then maintained at a pressure of 760 mm. of mercury by putting more gas in or taking some out by means of a mercury leg and the process was continued until absorption stopped as indicated by the absence of any change in the mercury manometer connected to the system. Solutions of different concentrations were then prepared by adding different amounts of the saturated liquid to the pure one in different test tubes with standard B14 necks and weighing. Care was taken that no gas escaped from these solutions by filling the test tubes nearly to the stopper mark and stoppering immediately with standard stoppers. The interferometric readings corresponding to these solutions of known concentrations with reference to the pure liquid was then determined as will be described presently and a graph of interferometric readings vs. concentration was plotted which served as a ready reference for reading out concentrations of unknown solutions directly from this curve if the corresponding interferometric reading was determined.

The interferometer is provided with two identical transparent cells fitted side by side in a brass frame. One of these cells is filled with the reference liquid while the other contains

the solution to be examined. That being done, the two cells are covered by means of two rectangular pieces of glass and the whole set-up put into the water chamber which is maintained at a constant temperature. The water is stirred and the cells allowed to stand until, on looking through the eye-piece, the two sets of interference pattern show no curvature. The screw-head carrying the circular scale is then adjusted until the two interference patterns seen with the eye-piece are exactly matched and the corresponding reading on the scales is noted. This reading minus the reading taken when both the cells contain pure liquid (which should be zero if the instrument is properly adjusted) is a function of the refractive index of the solution, which in turn is a function of its concentration. Thus by determining this reading, the concentration of a solution can be determined with the aid of the calibration curve drawn previously. It should be noted, however, that the liquid which is used as a reference and the liquid from which the solution is made must be from the same stock, as even a slightest change in fractionation conditions may mean an error of a number of divisions on the circular scale. For this purpose, sufficient quantities of the liquid were acquired and fractionated and the same stock was used throughout for experiments with that liquid. The cells were cleaned and dried before each determination and the reference liquid was taken always from the same bottle.

Results

Experiments were carried out at 25°C with ethylene and


GRAPH No. 1
CALIBRATION OF INTERFEROMETER
SYSTEM: DEKALIN-ETHYLENE
TEMPERATURE 20°C.
INTERFEROMETER READING
500
450
400
350
300
250
200
150
0
10
20
30
40
50
60
70
80
90
100
PERCENT SATURATED

hydrogen as the gases and dekalin and toluene as the liquids. From the concentration of the solutions of the two chambers determined at the conclusion of each diffusion run, and the measured cell constant, the corresponding diffusivity was calculated by substitution in equation 27.

The following is a sample calculation of diffusion coefficient of gases in liquids from rate measurements.

Run No. 315 Ethylene System. Ethylene - Dekalin

Temperature of Experiment. 25°C. Time of equilibrium. 4 hrs.

Cell No. 1

Volume of Upper chamber. 71.5

Volume of Lower chamber. 77.6

Initial concentration of the solution in the upper chamber. 37.2% saturated.

Initial concentration of the solution in the lower chamber. 0%

Intefferometric reading of the solution in the upper chamber at the end of a diffusion run. 269

Interferometric reading of the solution in the lower chamber at the end of a diffusion run. 170

Hence final concentration of the solution in the upper chamber. 33.3% saturated.

Hence final concentration of the solution in the lower chamber. 3.6% saturated.

The cell constant. .194/cm^2.

Duration of the run = 17 hours.

Hence the diffusion coefficient $D = \frac{1}{t \times K} \log_e \frac{C_{f1} + C_{f2} \times \frac{V_2}{V_1}}{C_{f1} - C_{f2}}$

$$= \frac{1}{17 \times 3600 \times .194} \log_e \frac{33.3 + 3.6 \times \frac{77.6}{71.5}}{33.3 - 3.6}$$

$$= \frac{1}{17 \times 3600 \times .194} \log_e 1.252$$

$$= 1.897 \times 10^{-5} \text{ cm}^2/\text{sec.}$$

Mean concentration at which the diffusion takes place

$$= \frac{37.2 + 0}{2} = 18.6\% \text{ saturated.}$$

(Assuming that D varies linearly with concentration and the system being closed.)

Similarly, the diffusion coefficients were calculated for other runs. Following tables give the results obtained in this series of experiments.

TABLE III.

System: Ethylene - Dekalin.

Temperature: 25°C.

TABLE III /

TABLE III.

Diffusion coefficients of Ethylene in Dekalin at 25°C.

Pressure: Atmospheric.

Time of equilibrium = 4 hours.

Cell Number	Time of Diffusion (hours)	Concentration in terms of percentage saturation				Mean concentration at which diffusion takes place	Diffusion coefficient $cm^2/sec \times 10^5$
		Initially in Lower chamber	Initially in Upper chamber	Finally in Lower chamber	Finally in Upper chamber		
1	19.0	Nil	34.2	3.30	30.60	17.1	1.74
1	18.0	Nil	25.4	2.70	22.50	12.7	1.99
1	18.0	Nil	40.0	4.20	35.40	20.0	1.97
1	22.5	Nil	34.0	4.20	29.40	17.0	1.90
2	19.5	Nil	39.8	4.50	35.10	19.9	1.83
1	18.5	Nil	37.9	4.20	33.30	19.0	2.06
2	43.0	Nil	31.2 ?	6.30	24.60	15.6	1.66
1	42.0	Nil	29.0	6.00	22.50	14.5	1.93
2	19.0	Nil	22.7	2.70	19.90	11.4	1.97
2	19.0	Nil	16.3	2.10	14.10	8.2	2.14
3	18.0	Nil	33.1	4.50	28.50	16.6	2.12
2	18.75	Nil	31.4	3.30	27.90	15.7	1.71
1	17.0	Nil	36.6	3.30	33.00	18.3	1.76
3	18.25	Nil	41.5	5.10	36.30	20.8	1.86
1	17.5	Nil	39.7	4.20	35.10	19.9	2.05
2	18.75	Nil	46.5	5.10	41.10	23.3	1.82
3	18.0	Nil	47.1	5.40	39.60	23.6	1.77
1	17.0	Nil	37.2	3.60	33.30	18.6	1.90
2	16.5	Nil	62.7	6.00	56.40	31.4	1.80
3	15.5	Nil	61.9	5.70	56.10	31.0	1.54
1	65.5	Nil	22.4	6.30	15.60	11.2	1.93
3	18.25	Nil	31.9	4.50	27.30	16.0	2.09
3	19.0	Nil	45.1	6.0	39.0	22.6	1.85

TABLE IV

Diffusion Coefficients of Ethylene in Toluene at 25°C.

Pressure: Admospheric. Time of Equilibrium: 4 hours

Cell No.	Time of Diff. hrs.	Concentration in terms of percentage saturation					Diffusion Coefficient $cm^2/sec. \times 10^5$.
		Initially in lower chamber C_{i2}	Initially in upper chamber C_{ii}	Finally in lower chamber C_{f2}	Finally in upper chamber C_{fi}	Mean conc. at which diff. takes place. C_o	
1	19.5	Nil	17.0	3.30	13.45	8.5	4.08
2	43.0	Nil	54.0	19.45	33.60	27.0	4.27
1	19.0	Nil	52.6	10.35	41.40	21.3	4.10
2	18.0	Nil	46.9	10.00	36.35	23.5	4.42
1	19.0	Nil	44.8	10.15	33.80	22.4	4.54
2	18.0	Nil	46.5	9.30	36.70	23.3	3.82
1	19.0	Nil	67.1	12.95	53.10	33.6	3.94
1	19.0	Nil	61.8	13.10	47.55	30.9	4.42
2	18.0	Nil	45.8	9.80	35.50	22.9	4.38
1	19.0	Nil	27.5	5.50	21.55	13.8	4.08
2	20.0	Nil	25.2	5.50	19.45	12.6	4.02
1	19.0	Nil	17.2	3.75	13.10	8.6	4.32
2	18.0	Nil	15.3	2.95	12.25	7.7	3.64
1	19.0	Nil	29.3	6.50	22.25	14.7	4.45
2	16.5	Nil	37.7	8.40	28.90	18.9	4.30
1	19.0	Nil	40.2	8.25	31.20	20.1	4.02
2	18.0	Nil	38.7	7.70	30.65	19.4	3.99
1	19.0	Nil	25.8	5.35	20.00	12.9	4.02
2	18.0	Nil	25.3	5.35	19.65	12.7	4.12
1	19.25	Nil	23.7	5.00	18.25	11.9	4.10
1	19.0	Nil	17.2	3.60	13.30	8.6	4.15
2	18.0	Nil	22.6	4.80	17.55	11.3	4.15
1	19.0	Nil	15.1	3.30	11.55	7.6	4.33
2	18.0	Nil	13.6	2.95	10.50	6.8	4.27
2	18.0	Nil	8.3	1.55	6.70	4.2	3.49
1	19.0	Nil	35.8	6.85	28.40	17.9	3.89
2	18.0	Nil	34.4	7.55	26.50	17.2	4.50
1	19.0	Nil	19.1	3.60	15.15	9.6	3.80
2	18.0	Nil	19.1	3.80	15.15	9.6	3.96

TABLE V.

Diffusion Coefficients of Hydrogen in Dekalin at 25°C.
Pressure: Atmospheric. Time of Equilibrium: 4 hours.

Cell No.	Time of diff. hrs.	Concentration in terms of percentage saturation					Diffusion Coefficient $cm^2/sec. \times 10^5$.
		Initially in lower chamber C_{i1}	Initially in upper chamber C_{i2}	Finally in lower chamber C_{f1}	Finally in upper chamber C_{f2}	Mean conc. at which diff. takes place. C_o	
1	19.0	87.60	Nil	72.20	16.70	43.8	3.45
2	18.0	88.10	Nil	72.20	16.70	44.1	3.47
1	19.0	87.60	Nil	72.20	16.70	43.8	3.45
2	18.0	88.10	Nil	72.20	16.70	44.1	3.47
2	18.0	88.10	Nil	72.20	16.70	44.1	3.47
2	18.0	88.10	Nil	72.20	16.70	44.1	3.47

TABLE VI.

Diffusion Coefficients of Hydrogen in Toluene at 25°C.
Pressure: Atmospheric. Time of Equilibrium: 4 hours.

Cell No.	Time of diff. hrs.	Concentration in terms of percentage saturation					Diffusion Coefficient $cm^2/sec. \times 10^5$.
		Initially in lower chamber	Initially in upper chamber	Finally in lower chamber	Finally in upper chamber	Mean conc. at which diff. takes place.	
1	19	65.9	Nil	46.50	21.00	33.0	7.16
2	18	66.5	Nil	46.50	21.00	33.3	7.17
1	19	90.8	Nil	64.00	29.00	45.4	7.16
2	18	91.6	Nil	64.00	29.00	45.8	7.17
1	19	90.8	Nil	64.00	29.00	45.4	7.16
2	18	91.6	Nil	64.00	29.00	45.8	7.17

A new technique for the measurement of diffusion coefficient of gases in liquids.

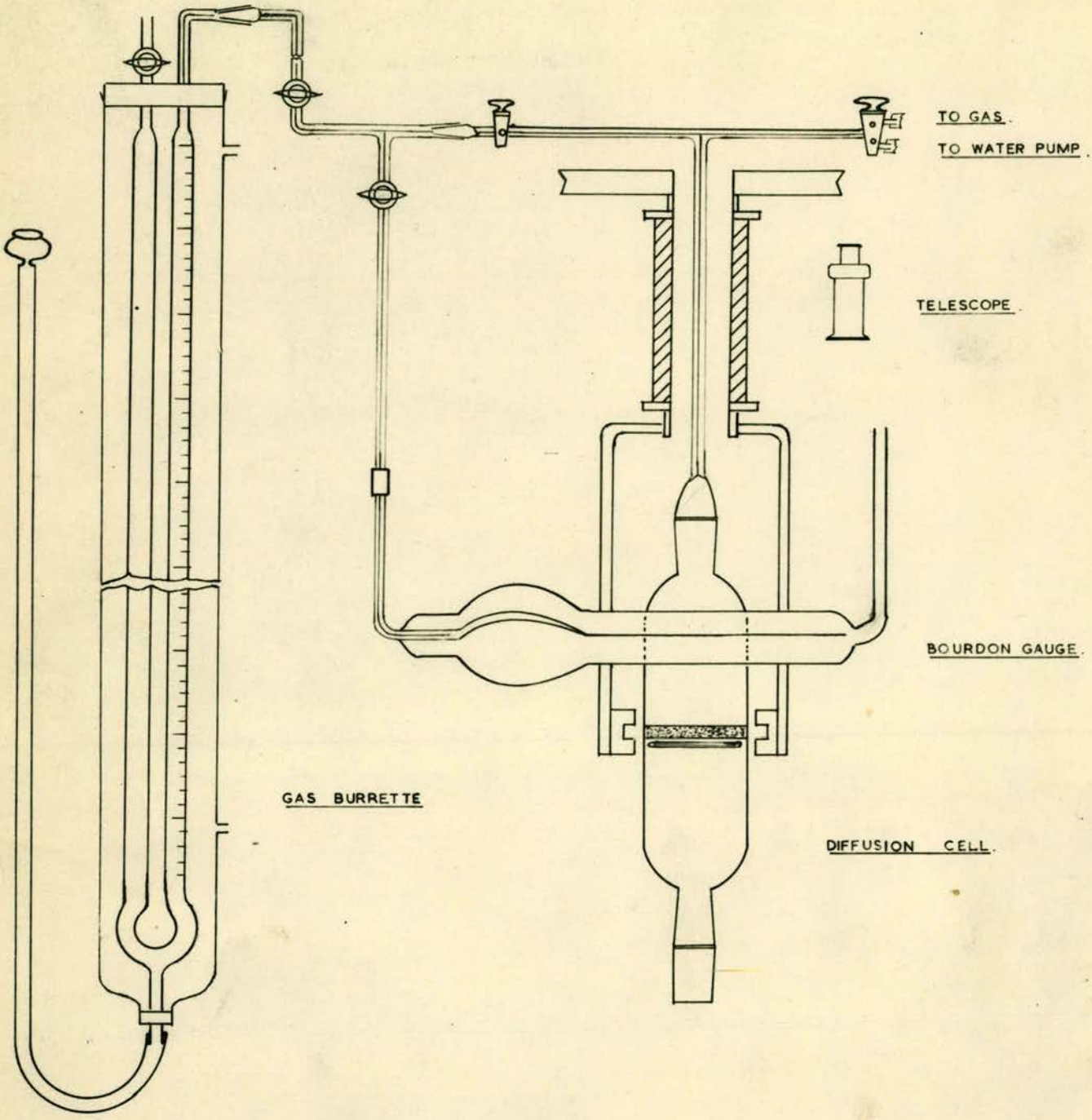
In the light of the experience gained from the above experiments, it was realised that it might have been better if some method could be developed in which concentration changes could be measured as diffusion proceeded. Two serious difficulties were encountered in the experiments described above, namely, the measurement of diffusivity from highly concentrated solutions to pure liquid was not possible as the former lose their gas very rapidly in course of handling for the experiment. Even if it were prevented, the concentration of the solution became considerably less in course of the period of equilibrium and even lesser during the course of a diffusion run. Since in mass transfer experiments, diffusion usually takes place from a saturated layer into a nearly pure liquid, the diffusion coefficient measured in the above experiments is not the one which should be applicable under such conditions as has already been remarked. Secondly, the time allowed for diffusion in such experiments is so much more than that allowed in mass transfer operations that these values of diffusivity would seem to lead to unjustified conclusions. This shortcoming, however, would not apply to the systems for which the diffusivity does not vary significantly with concentration and consequently with the time of contact.

Keeping this in mind, it was thought that if diffusion took place from a solution which was maintained saturated into an initially pure liquid, the latter being allowed to change in

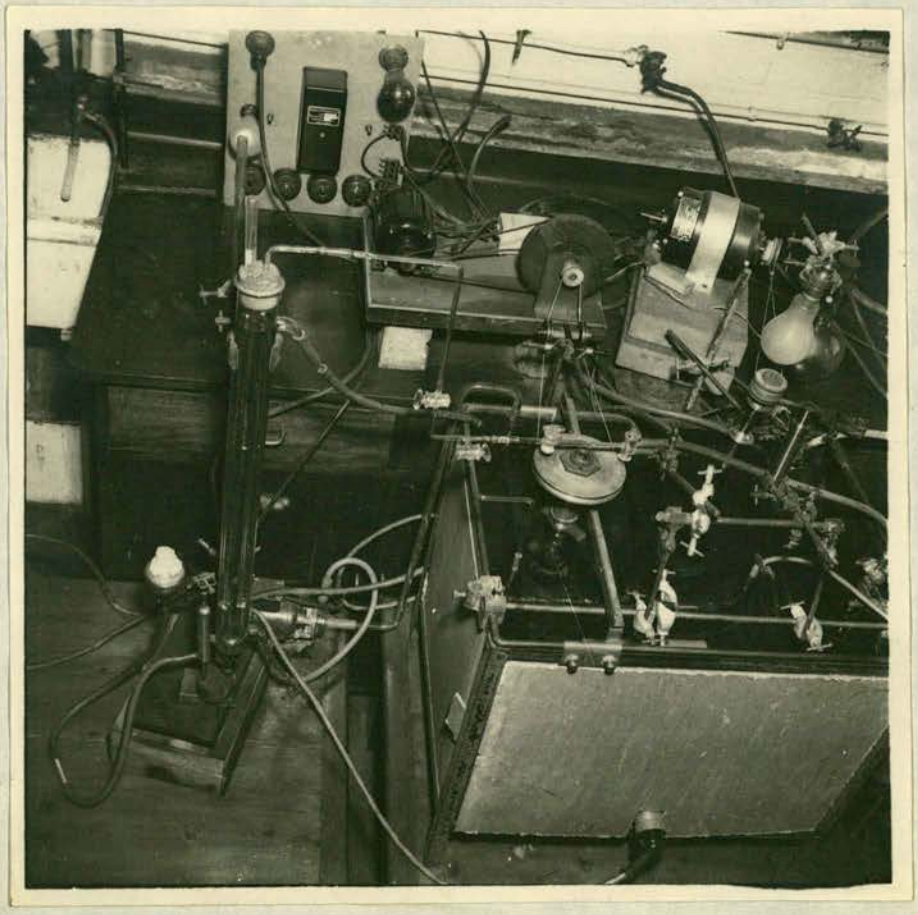
concentration due to diffusion, it would not be very far from what really happens in mass transfer operations. In the diffusion cell used above, if the lower chamber contains pure liquid and the upper is filled up with the gas in question with a thin layer of liquid on the diaphragm, it will not be very unreasonable to assume this layer to be saturated at the temperature and pressure of the gas. If these are maintained constant, the situation will correspond to diffusion from a saturated liquid into a liquid which is sensibly constant in composition over small time intervals below the diaphragm. That is to say, we shall have diffusion from a liquid layer of constant composition into a liquid below the diaphragm which is initially of nearly zero concentration and may be assumed to remain so for the short time interval over which the coefficient is measured because of comparatively large volume of the liquid and in any case, when the solubility of the gas is small. In other words, after equilibrium is established, a stationary state will exist within the diaphragm, especially so when the time interval over which the diffusivity is measured is short or the solubility of the gas is low and equation (20) for steady state diffusion should be applicable. Otherwise, the upper chamber may be supposed to be completely filled up with the saturated solution (as the effect is nearly the same) the concentration of which is maintained constant and the coefficient of diffusion calculated on the assumption of the existence of a quasi-stationary state and therefore by the application of equation (27). In any case, one can apply both the equations

and compare the results to see which assumption is nearer the truth.

Assuming that the thin layer of liquid above the diaphragm is maintained saturated by the presence of pure gas at the temperature and pressure of the experiment, it follows that any decrease in the amount of gas in the upper chamber will be equal to that passed into the liquid in the lower chamber by diffusion (as the mass flow has been eliminated here). Thus by devising a method of measuring the decrease in the amount of gas in the upper chamber continuously, it will be possible to measure diffusion coefficients over short time intervals and at the same time determining its variation with concentration. This will yield diffusivity values over a wide concentration range in a single experiment and will save much time compared with the former method. It must be admitted, however, that this method does not lend itself to the measurement of diffusivity from an unsaturated solution, the maintenance of which in the layer above the diaphragm is not allowed by the procedure, at any rate to maintain it at a known value except the limiting one throughout the course of an experiment. This, however, does not concern our purpose as we are interested mainly in measuring rates of diffusion from a saturated solution. With these ideas, the conventional diaphragm diffusion cell was redesigned to suit gas-liquid systems, a description of which, together with the method of procedure, follows.



THE NEW APPARATUS.



PHOTOGRAPH OF THE
NEW APPARATUS

The apparatus

The cells used in these experiments were the same as in the previous ones except that the upper end of the cell was connected by means of a standard B14 cone to a gas measuring system instead of being stoppered. As shown in the diagram, the upper end of the cell was connected by means of a narrow capillary which passed through the hollow shaft of the pulley carrying the magnets to a water pump, to a gas burrette, to a Bourdon gauge and to the gas cylinder. Each of the last four may be connected or disconnected with the diffusion cell by means of stop cocks. The gas burrette is graduated in tenths of a cubic centimeter and the pressure and volume of the gas inside it may be adjusted by means of a mercury leg. The burrette is provided with a jacket through which water from the thermostat circulates maintaining the gas inside the burette at the temperature of the experiment. Since all the connections are made with very narrow capillary, the volume contained therein is negligible compared to that of the diffusion cell and of the gas burrette so that all the gas contained in the apparatus may be safely assumed to be at the thermostat-temperature. All connections involving capillary tubing were made with standard A7 joints except that with the Bourdon gauge where a very small length of rubber tubing was used in conjunction with the gas burrette to keep the system at constant pressure so that the volume of the gas diffused can be read off directly from the graduated limb of the burrette. The Bourdon gauge is maintained at constant temperature by fixing it inside the thermostat.

The procedure

The cell was cleaned, dried and the lower chamber was filled with the pure liquid which was allowed to drain through the sinter so that no air was left inside the pores. The stirrer was then put inside and the chamber filled again with the degassed liquid at the temperature of the experiment and stoppered, avoiding gas bubble inside the cell. Any liquid in the upper chamber was then drained and the cell allowed to stand in the thermostat for about ten minutes to make up for any temperature loss. The cell was put on its seat and connected by means of capillary leads to the burrette, to the Bourdon gauge, to the gas cylinder and to the water pump. The stop cock leading to the Bourdon gauge was then closed as also that leading to the gas supply and the other end of the Bourdon gauge was also disconnected from the atmosphere by closing the same. The atmospheric pressure at that point was noted as also the reading of the Bourdon gauge pointer on the telescope scale. The upper chamber of the cell was then evacuated by means of the water pump and refilled with the gas from the cylinder. This process was repeated a number of times to ensure that the air inside the cell was completely replaced by the gas. In the last refilling, the gas was admitted to a slightly higher pressure than the atmospheric which was allowed to fall to the atmospheric by momentarily opening the system to the atmosphere. At that point the magnetic stirrer was started, the stop cock leading to the Bourdon gauge opened and readings of the Bourdon gauge pointer and the gas burrette taken. This instant was taken as the start of a diffusion run. Readings of the

Bourdon gauge pointer on the telescope scale were taken every five minutes to an hour interval depending on the system under observation and the Bourdon gauge pointer brought back to the original reading by letting more mercury in the burrette so that a constant pressure was maintained throughout the period of the run. When this was attained, the reading on the gas burrette showed the volume of gas remaining within the apparatus and the difference between that reading and the reading at the beginning of the interval corresponded to the volume of the gas diffused during the interval. From the knowledge of the volume of the gas diffused during a specific time interval reduced to normal temperature and pressure, of the solubility of the gas in the liquid at that temperature and pressure and of the value of the ratio of the effective pore area to the length($A/_L$) of the sintered disc or of the cell constant, the diffusion coefficient was calculated by substitution in equation 20 or 27 on the assumption of a stationary or a quasi-stationary state respectively. The ratio A/L was calculated from the knowledge of the cell constant and of the volumes of the two cell compartments and the application of equation 26a. All the joints except the lower end of the cell (in which case the liquid contained therein itself acted as a lubricant) were lubricated with vaseline and made air tight. All liquids used were completely degasified as even a trace of dissolved gas gave rise to bubbles during the evacuation of the apparatus and spoiled the whole experiment. Various curves are drawn to show the variation in the rates of diffusion with time and hence with concentration in various systems, any two points on which

correspond to conditions at the two instants. From the amount of gas diffused between these instants, the diffusivity during the same concentration interval may be calculated.

Following table shows the solubility of the gases concerned in the liquids which will be used in the computation of the diffusion coefficients. The graph on the left shows the variation of solubility of the systems with temperature whenever possible.

TABLE VII.

Data on solubilities in vol. gas at N.T.P. per vol. liquid.

Pressure: 1 atmosphere.

System	Toluene - Hydrogen	Water - Hydrogen	Water - Carbon Dioxide	Water - Sulphur Dioxide	Water - Ethylene
Ref.	93	94	94	94	94
Temp.°C					
0	-	0.0214	1.713	79.79	0.226
5	-	0.0204	1.424	67.48	0.191
10	0.0642	0.0195	1.194	56.65	0.162
15	-	0.0188	1.019	47.28	0.139
20	0.0700	0.0182	0.878	39.37	0.122
25	-	0.0175	0.759	32.79	0.108
30	0.0735	0.0170	0.665	27.16	0.098
35	-	-	-	22.49	0.078 (37.5°C)
40	0.0755	0.0164	0.530	18.77	-
50	0.0760	0.0161	0.436	15.60	-
60	0.0750	0.0160	0.359	-	-
70	0.0720	0.0160	-	-	-
80	0.0660	0.0160	-	-	-
90	0.0567	0.0160	-	-	-
100	0.0385	0.0160	-	-	-

TABLE VII (Contd.)

Data on solubilities in vol. gas at N.T.P. per vol. liquid.

Pressure: 1 atmosphere.

System	Benzene - Ethylene	Xylene - Ethylene	Dekalin - Ethylene	Toluene - Ethylene
Ref.	94	94	91	91
Temp.°C				
0	-	5.95	-	-
20	3.01 (22°C)	3.80	2.416	2.851
35	2.655	-	-	-
40	-	3.03	-	-
50	2.482	-	-	-

Results

Following is an example of calculation of diffusivity from rate measurements by the technique described above.

System: Ethylene - Toluene.

Temperature 25°C.

Pressure 29.82" of Mercury.

Cell Number 4.

Cell constant .108/cm^2 (Table II)

V_1 = 53.3 ml. V_2 = 59.8 ml. (Table I).

Hence $A/L = \frac{K}{\frac{1}{V_1} + \frac{1}{V_2}} = \frac{.108}{1/53.3 + 1/59.8} = \underline{3.04 \text{ cm.}}$

Solubility of Ethylene in Toluene at 25°C and 1 atmosphere partial pressure = 3.25 ml. at N.T.P./ml. of liquid.

Time (in minutes)	Volume of Ethylene diffused at 25°C and 29.82" of Mercury p.p.
0	0
30	0.65
60	1.40
90	2.10
120	2.80
150	3.50
180	4.30
210	4.90
240	5.60
270	6.30
300	7.00
330	7.60
360	8.40

The graph of the volume of gas diffused vs. time plotted before shows a steady diffusion rate of 1.4 ml/hour during the first six hours of diffusion. (Any discrepancy in the value noted above is due to error in observation and hence ignored.) Thus, we have,

Time interval t = 30 minutes.

Volume of gas diffused = .7 ml. at 25°C and 29.82" of Mercury p.p.

Hence the volume of the gas diffused at N.T.P.s = 0.639 ml.

Concentration of the gas in the liquid in the lower chamber at the end of the interval $= \frac{0.639}{59.8}$ ml/ml $= 0.0107$ ml/ml.

Hence mean concentration of the liquid in the lower chamber during the interval $= \frac{0 + .0107}{2}$ ml/ml

$= .00535$ ml/ml.

Hence the concentration gradient causing the diffusion during the interval $C_e = 3.25 - .00535$

$= 3.24465$ ml/ml.

From equation 20, during the steady state, the diffusion coefficient is given by the relation,

$$D_{S.S.} = \frac{S}{t.A/L\ C_e}$$

$$= \frac{0.639}{30 \times 60 \times 3.04 \times 3.24465}$$

$$= 3.60 \times 10^{-5}\ cm^2/sec.$$

Mean concentration of the liquid at which the diffusion takes place $= \frac{3.25 + .00535}{2}\ ml/ml$

$= 1.628\ ml/ml.$

On the assumption of a quasi-stationary state, we have, from equation 27,

$$D_{Q.S.S.} = \frac{1}{t\ ,\ K} \log_e \frac{(C_1 - C_2)_o}{(C_1 - C_2)f.}$$

Here, the concentration gradient at the start of the interval $= 3.25 - 0 = 3.25\ ml/ml.$ and the concentration gradient at the end of the interval $= 3.25 - .0107 = 3.2393\ ml/ml.$

Hence $D_{Q.S.S.} = \frac{1}{30 \times 60 \times .108} \log_e \frac{3.25}{3.2393}$

$$= 1.648 \times 10^{-5}\ cm^2/sec.$$

For the next 30 minutes' interval, calculations are made as follows:-

Time interval t = 30 minutes.

Volume of gas diffused = .7 ml. at 25°C and 29.82" of Mercury p.p.

Hence the volume S of the gas diffused during the interval at N.T.P. = 0.639 ml.

Concentration of the gas in the liquid in the lower chamber at the beginning of the interval $= \frac{0.639 ml}{59.9}/ml = 0.0107\ ml/ml.$ At the end of the interval $= \frac{1.278}{59.9}\ ml/ml = 0.0214\ ml/ml.$

Hence the mean concentration of the solution in the lower chamber during the interval $= \frac{0.0107 + 0.0214}{2}$

$= 0.01605\ ml/ml.$

Hence the concentration gradient causing the diffusion during the interval L_e = 3.25 - 0.01605 = 3.23395 $ml/_{ml}$ and

$$D_{S.S} = \frac{0.639}{30 \times 60 \times 3.04 \times 3.23395} \text{ cm}^2/\text{sec.}$$

$$= 3.62 \times 10^{-5} \text{ cm}^2/\text{sec.}$$

Mean concentration of the liquid over which the diffusion takes place = $\frac{3.25 + .01605}{2}$ $ml/_{ml}$

= 1.636 $ml/_{ml}$.

For $D_{Q.S.S.}$ we have,

Concentration gradient at the start of the interval = 3.2393 $ml/_{ml}$.

Concentration gradient at the end of the interval = 3.25 - .0214 = 3.2286 $ml/_{ml}$.

Hence $D_{Q.S.S.} = \frac{1}{30 \times 60 \times .108} \log_e \frac{3.2393}{3.2286}$

$$= 1.648 \times 10^{-5} \text{ cm}^2/\text{sec.}$$

It will be seen from Graph 2 that in some cases, e.g., in the case of a viscous liquid like dekalin, equilibrium is not established instantly and the start of the run therefore is taken when the curve becomes smooth. In case of very slightly soluble gases, the volume of the gas diffused in short time intervals cannot be measured very accurately and therefore the interval over which the diffusivity is measured is considerably extended.

The following tables show the results of these experiments in detail.

TABLE VIII/

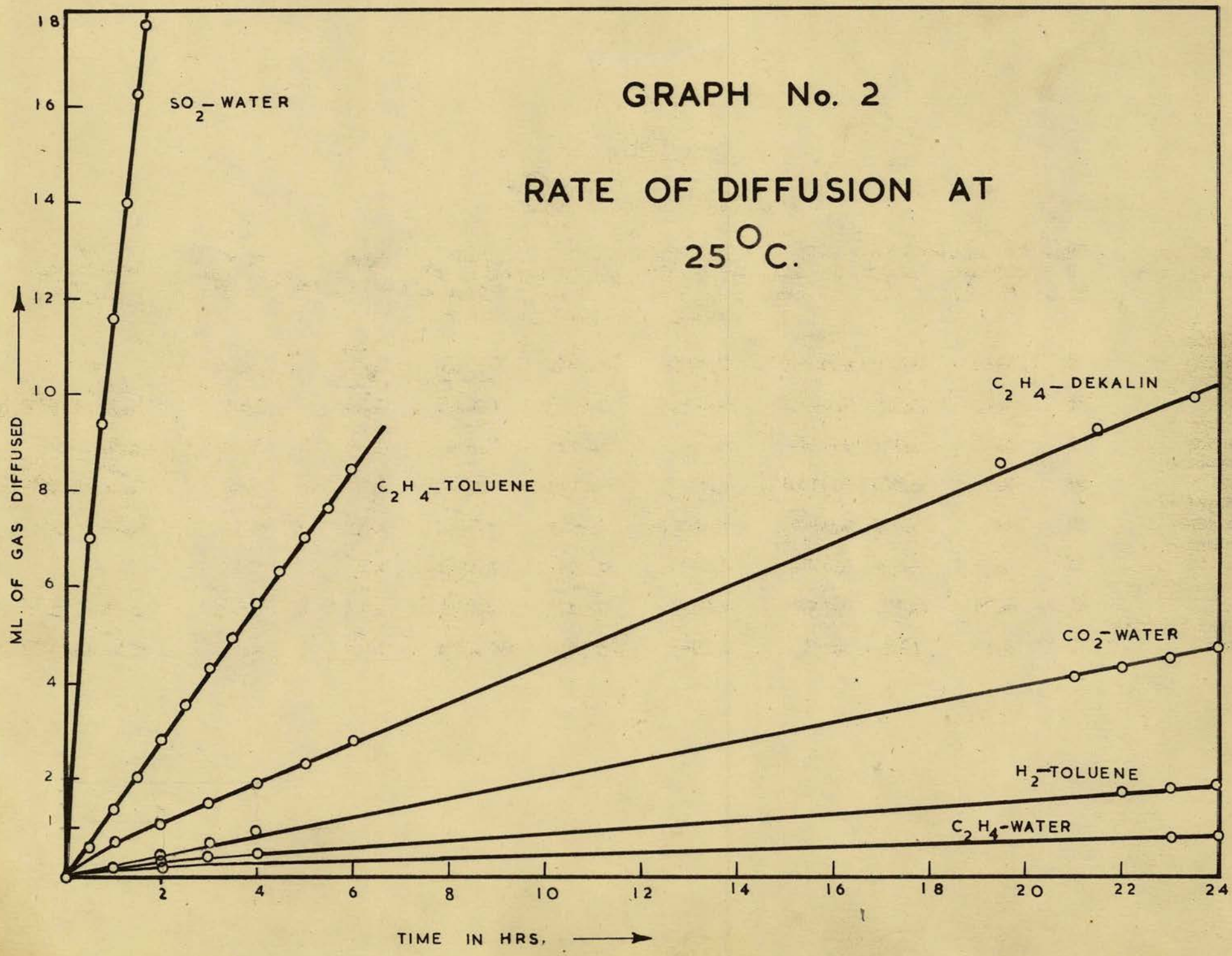

GRAPH No. 2
RATE OF DIFFUSION AT
25 °C.
SO2 – WATER
C2H4 – TOLUENE
C2H4 – DEKALIN
CO2 – WATER
H2 – TOLUENE
C2H4 – WATER
ML. OF GAS DIFFUSED
TIME IN HRS.
1
2
4
6
8
10
12
14
16
18
20
22
24

TABLE VIII.

Determination of D at 25°C.

System	Time t hrs.	Vol. of gas diffused S ml.	S at N.T.P. ml.	S/V v = vol. of liq.	Mean conc. C of liquid $\frac{1}{2}(0 + S/V)$ ml/ml.	C_e solubility ml/ml.	Mean conc. of diffusion ml/ml.	$D_{S.S.}$ $\times 10^5$ cm^2/sec.	$D_{Q.S.S.}$ $\times 10^5$ cm^2/sec.	D (ref.) literature $\times 10^5$ cm^2/sec.
Ethylene - Dekalin	1	0.42	0.372	0.00623	0.00312	2.3669	1.1881	1.44	0.746	-
Ethylene - Water	24	0.65	0.595	0.00996	0.00498	0.10302	0.0565	2.20	1.04	1.59 at 20°C (97)
Ethylene - Toluene	1	1.40	1.279	0.0214	0.0107	3.2393	1.6304	3.61	1.72	2.85 (89)
Hydrogen - Water	26	0.3	0.267	0.00446	0.00223	0.01533	0.00987	6.10	2.91	5.94 at 20°C (97)
Hydrogen - Toluene	20	1.4	1.272	0.0213	0.01065	0.0611	0.0412	9.52	4.52	5.61 (89)
Hydrogen - Dekalin	26	0.5	0.458	0.00766	0.00383	0.04867	0.02817	3.3	1.56	-
Carbon dioxide - Water	24	4.55	4.10	0.0686	0.0343	0.7247	0.3967	2.16	1.015	1.74 at 20°C (97)
Sulphur dioxide - Water	1	8.775	7.81	0.131	0.0655	32.7245	16.4278	2.18	0.978	1.47 at 20°C (97)

It will be seen from the table that the values calculated on the basis of existence of a quasi-stationary state are too low, showing that a steady state actually exists in the system. Hence in the following tables D is calculated on the basis of existence of a stationary state only.

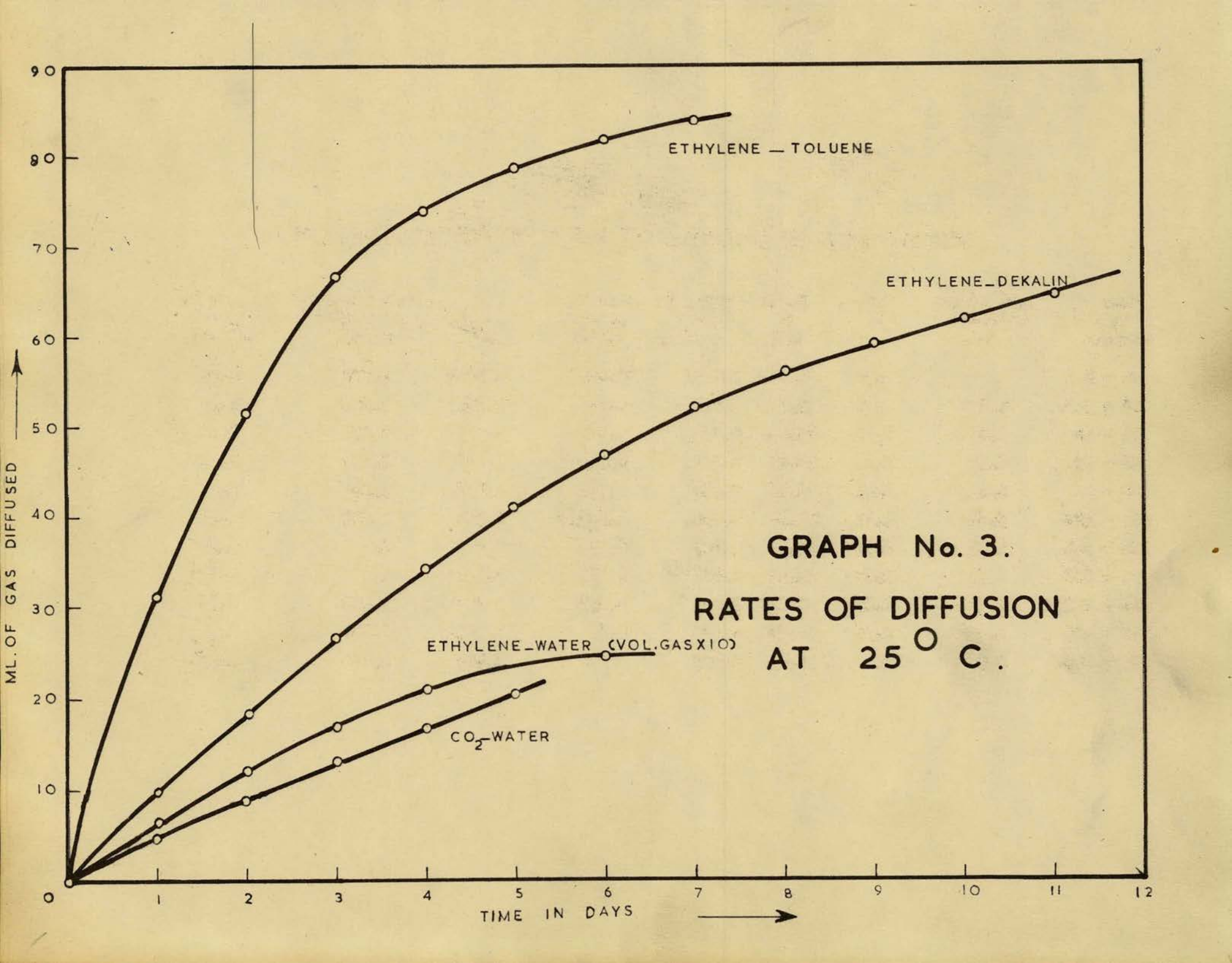

ETHYLENE — TOLUENE
ETHYLENE_DEKALIN
ETHYLENE_WATER (VOL.GAS X 10)
CO_2—WATER
GRAPH No. 3.
RATES OF DIFFUSION
AT 25° C.
ML. OF GAS DIFFUSED
TIME IN DAYS
0
10
20
30
40
50
60
70
80
90
1
2
3
4
5
6
7
8
9
10
11
12

TABLE IX.

Determination of the diffusion coefficient of Ethylene in Dekalin at 25°C.

Time in Hours	Vol. of gas diffused S ml.	S at N.T.P. ml.	Total S ml.	Total S / V ml/ml.	Mean conc. C of liq. ml/ml.	C_e ml/ml.	Mean conc. of diffusion ml/ml.	$D_{S.S.} \times 10^5$ $cm^2/sec.$
24 - 0	9.7	8.58	8.58	0.1435	0.0718	2.3012	1.422	1.44
48 - 24	8.8	7.79	16.37	0.274	0.209	2.164	1.291	1.37
72 - 48	8.0	7.08	23.45	0.393	0.334	2.039	1.354	1.32
96 - 72	7.7	6.81	30.26	0.506	0.450	1.923	1.412	1.35
120 - 96	6.8	6.01	36.27	0.606	0.556	1.817	1.465	1.26
144 - 120	5.63	4.98	41.25	0.690	0.648	1.725	1.511	1.10
168 - 144	4.45	3.94	45.19	0.757	0.724	1.649	1.549	0.91
192 - 168	3.75	3.32	48.51	0.811	0.784	1.589	1.579	0.795
216 - 192	3.20	2.83	51.34	0.858	0.835	1.538	1.604	0.701
240 - 216	2.65	2.34	53.68	0.900	0.879	1.494	1.626	0.596
264 - 240	2.45	2.17	55.85	0.935	0.918	1.455	1.646	0.568

TABLE X.

Determination of the diffusion coefficient of Ethylene in Toluene at 25°C.

Time in Hours	Vol. of gas diffused S ml.	S at N.T.P. ml.	Total S ml.	Total S / V ml/ml.	Mean conc. C of liq. ml/ml.	C_e ml/ml.	Mean conc. of diffusion ml/ml.	$D_{S.S.} \times 10^5$ $cm^2/sec.$
24 - 0	31.2	28.5	28.5	0.477	0.239	3.001	1.74	3.62
48 - 24	20.4	18.6	47.1	0.788	0.633	2.607	2.037	2.72
72 - 48	15.1	13.8	60.9	1.02	0.904	2.336	2.072	2.25
96 - 72	7.2	6.57	67.47	1.13	1.075	2.165	2.158	1.155
120 - 96	4.7	4.3	71.77	1.20	1.165	2.075	2.203	0.79
144 - 120	3.1	2.83	74.60	1.25	1.225	2.015	2.233	0.535
168 - 144	2.05	1.87	76.47	1.28	1.265	1.975	2.253	0.360

TABLE XI.

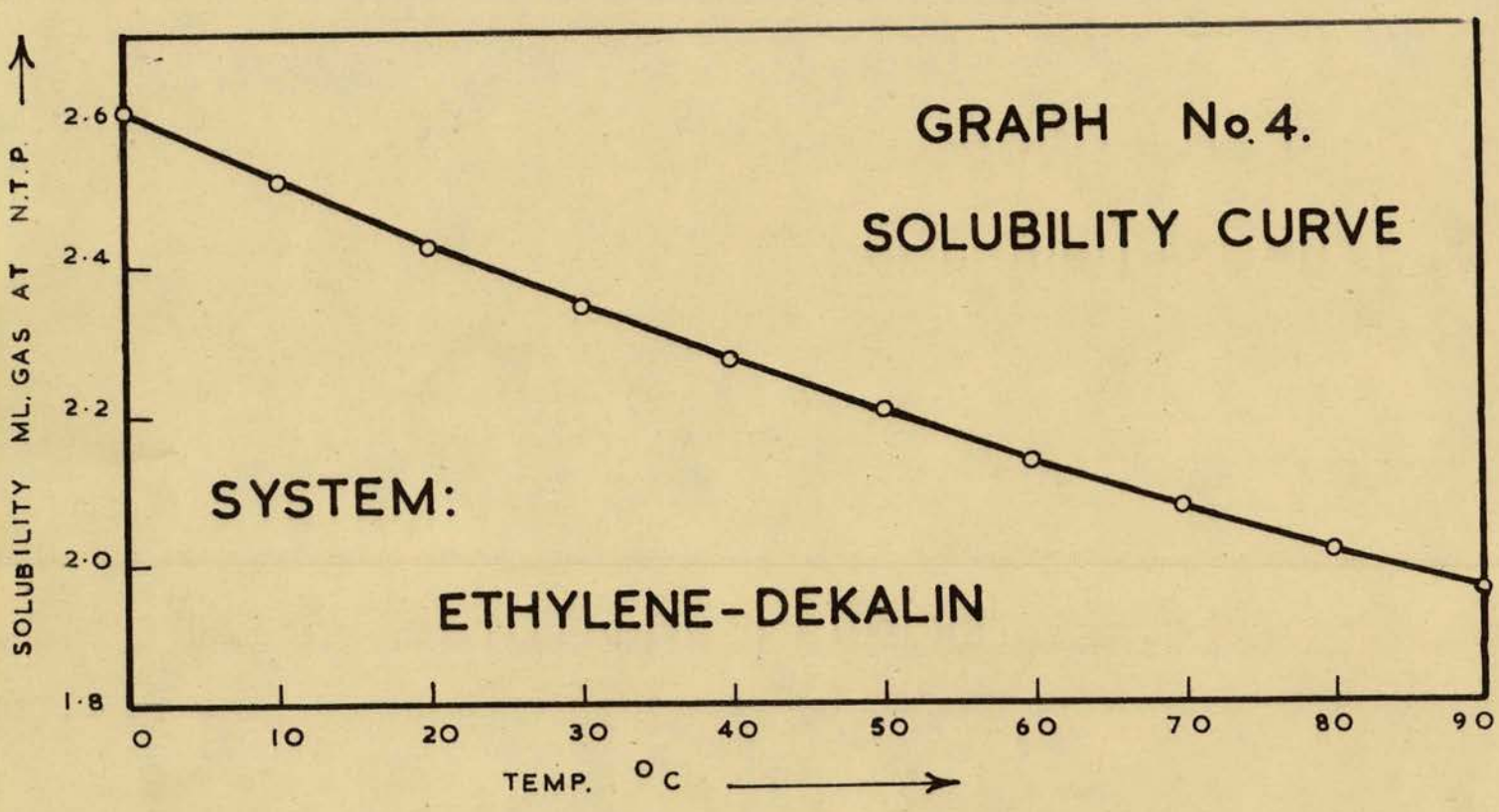
Determination of the diffusion coefficient of Ethylene in Water at 25°C.

Time in Hours	Vol. of gas diffused S ml.	S at N.T.P. ml.	Total S ml.	Total S / V ml/ml.	Mean conc. C of liq. ml/ml.	C_e ml/ml.	Mean conc. of diffusion ml/ml.	$D_{S.S.} \times 10^5$ $cm^2/sec.$
24 - 0	0.65	0.595	0.595	0.0096	0.00498	0.010302	0.0565	2.20
48 - 24	0.55	0.503	1.098	0.0184	0.01418	0.09382	0.0611	2.04
72 - 48	0.49	0.449	1.547	0.0259	0.02215	0.08585	0.0651	1.99
144 - 96	0.35	0.320	2.233	0.0374	0.0347	0.0733	0.0714	0.83

TABLE XII.

Determination of the diffusion coefficient of carbon dioxide in water at 25°C.

Time in Hours	Vol. of gas diffused S ml.	S at N.T.P. ml.	Total S ml.	Total S / V ml/ml.	Mean conc. C of liq. ml/ml.	C_e ml/ml	Mean conc. of diffusion ml/ml.	$D_{S.S.} \times 10^5$ $cm^2/sec.$
24 - 0	4.55	4.10	4.10	0.0686	0.0343	0.7247	0.3967	2.16
48 - 24	4.25	3.82	7.92	0.1326	0.1006	0.6584	0.4298	2.21
72 - 48	4.25	3.82	11.74	0.1966	0.1646	0.5944	0.4618	2.45
96 - 72	3.70	3.33	15.07	0.2520	0.2243	0.5347	0.4917	2.37
120 - 96	3.60	3.24	18.31	0.3060	0.2790	0.480	0.5190	2.57


GRAPH No. 4.
SOLUBILITY CURVE
SYSTEM:
ETHYLENE-DEKALIN
SOLUBILITY ML. GAS AT N.T.P.
2·6
2·4
2·2
2·0
1·8
0
10
20
30
40
50
60
70
80
90
TEMP. °C

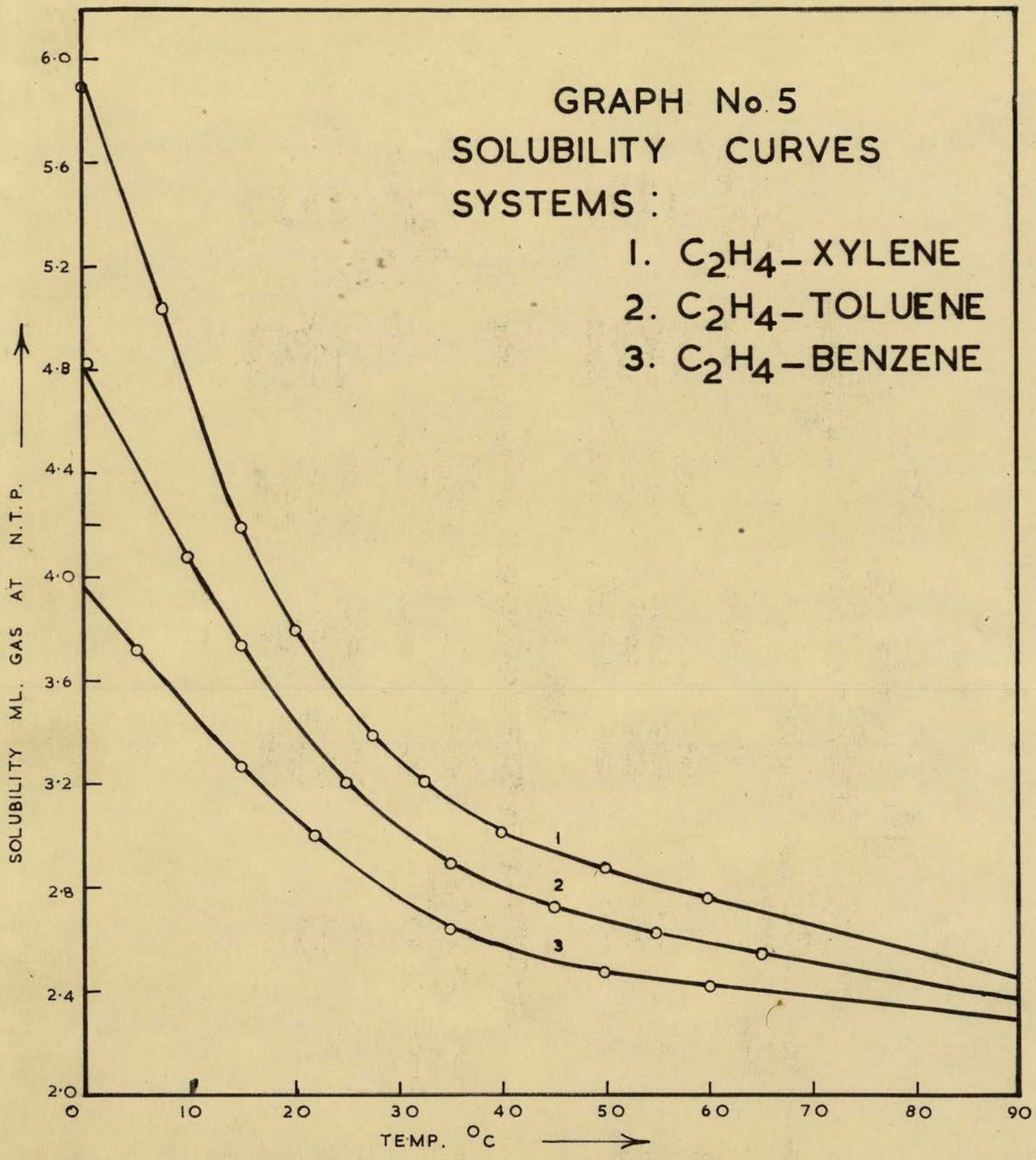

GRAPH No. 5
SOLUBILITY CURVES
SYSTEMS :
1. C_2H_4 – XYLENE
2. C_2H_4 – TOLUENE
3. C_2H_4 – BENZENE
SOLUBILITY ML. GAS AT N.T.P.
6·0
5·6
5·2
4·8
4·4
4·0
3·6
3·2
2·8
2·4
2·0
0
10
20
30
40
50
60
70
80
90
TEMP. °C
1
2
3

TABLE XIII.

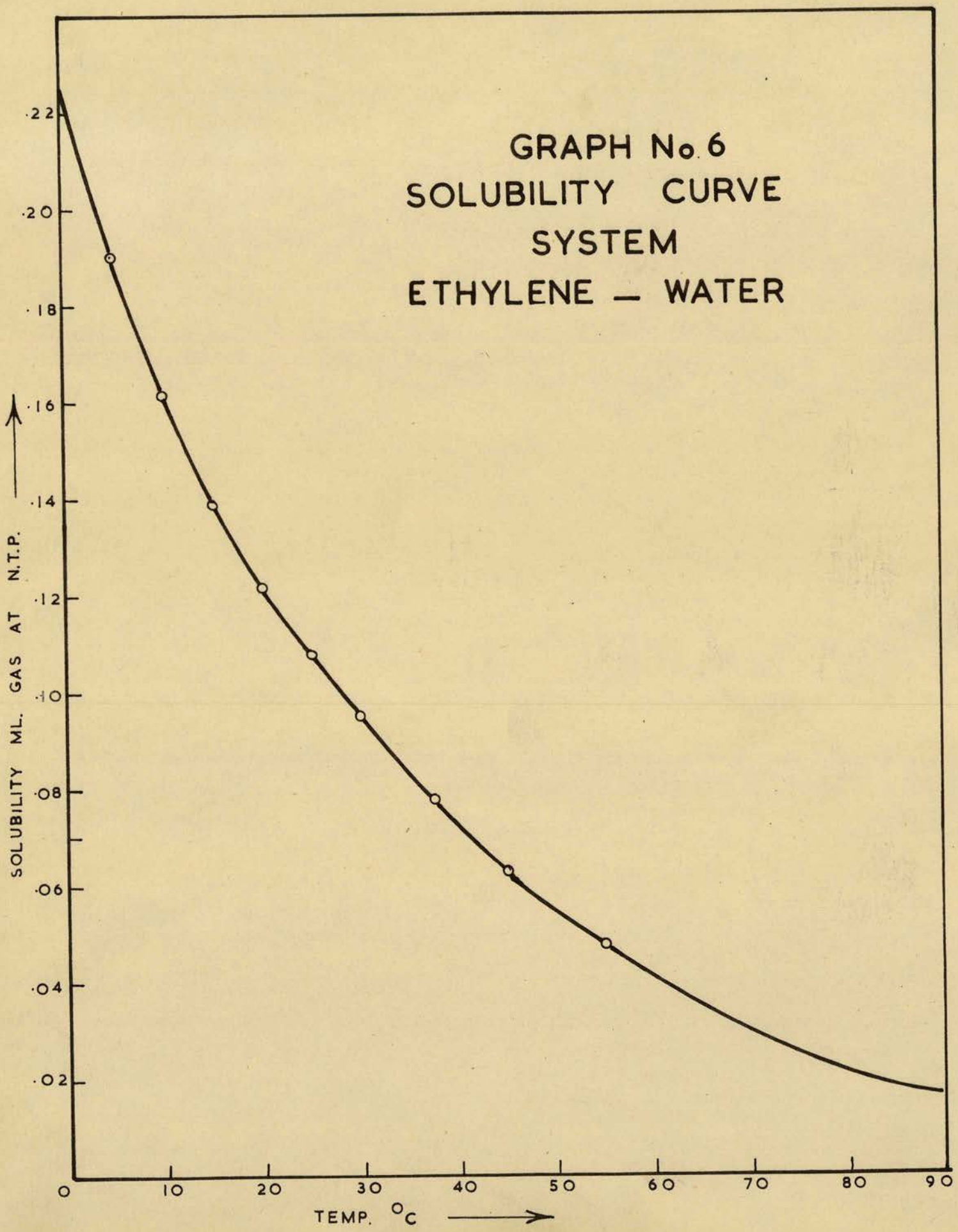
Determination of the diffusion coefficient of Ethylene in Dekalin.

Temp.	Time in Hours	Vol. of gas diffused S ml.	S at N.T.P. ml.	S/V ml/ml.	Mean conc. c of liq. ml/ml.	C_e ml/ml.	$D_{S.S.} \times 10^5$ $cm^2/sec.$
15°C	1	0.367	0.346	0.00579	0.00290	2.4571	1.29
25°C	1	0.42	0.372	0.00623	0.00312	2.3669	1.44
38°C	1	0.433	0.375	0.00628	0.00314	2.2719	1.51
62.5°C	1	0.415	0.382	0.00638	0.00319	2.1018	1.66

TABLE XIV.

Determination of the diffusion coefficient of Ethylene in Toluene.

Temp.	Time in Hours	Vol. of gas diffused S ml.	S at N.T.P. ml.	C_l ml/ml.	Mean conc. C of liq. ml/ml.	C_e ml/ml	$D_{S.S.} \times 10^5$ $cm^2/sec.$
15°C	1	1.40	1.325	0.0222	0.0111	3.7389	3.24
25°C	1	1.40	1.279	0.0214	0.0107	3.2193	3.61
35°C	1	1.40	1.261	0.0211	0.0106	2.8994	3.98
78°C	1	1.60	1.485	0.0248	0.0124	2.4476	5.54


GRAPH No. 6
SOLUBILITY CURVE
SYSTEM
ETHYLENE — WATER
SOLUBILITY ML. GAS AT N.T.P.
.22
.20
.18
.16
.14
.12
.10
.08
.06
.04
.02
0
10
20
30
40
50
60
70
80
90
TEMP. °C

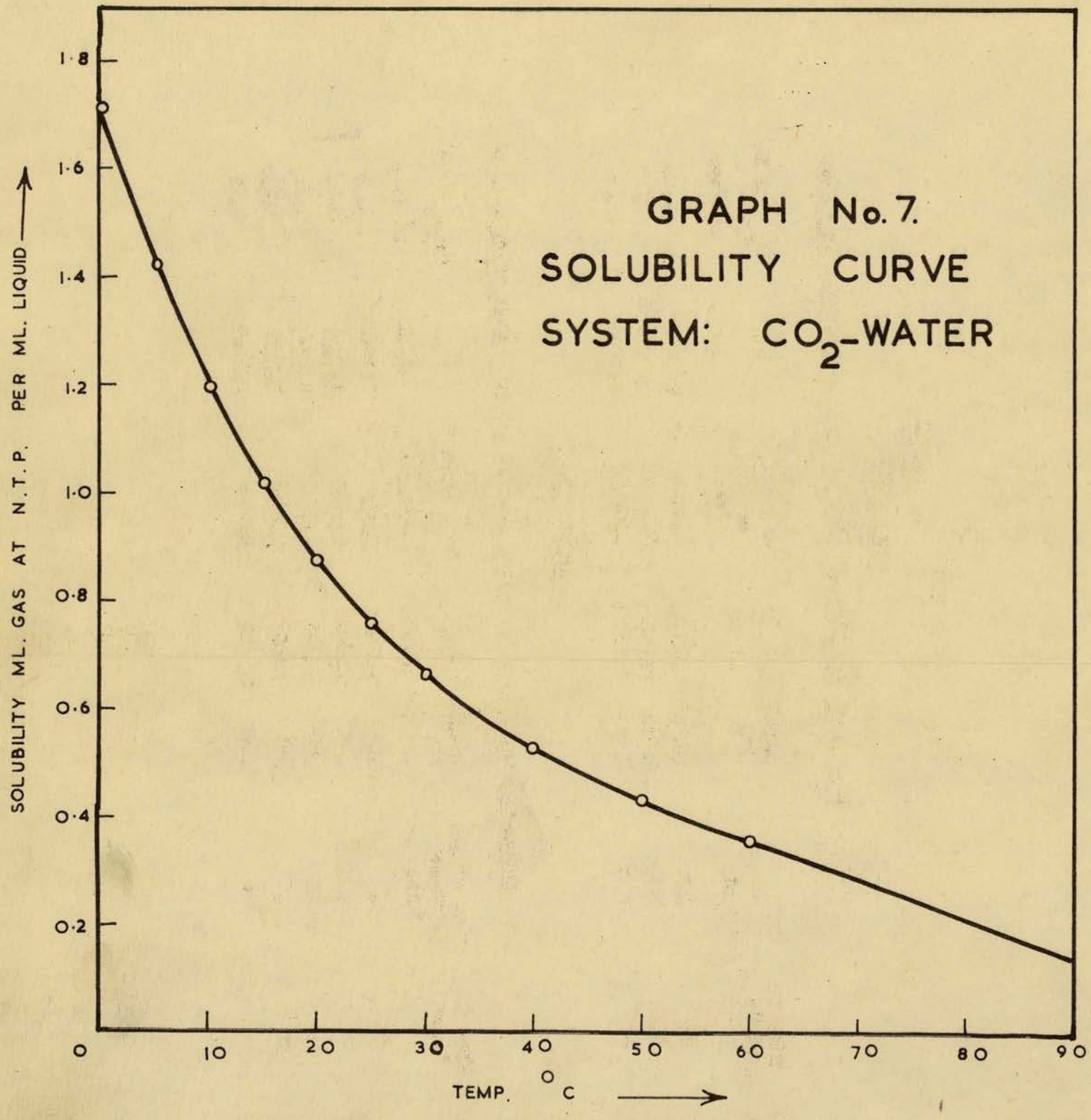

GRAPH No. 7.
SOLUBILITY CURVE
SYSTEM: CO_2-WATER
SOLUBILITY ML. GAS AT N.T.P. PER ML. LIQUID
1·8
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
0
10
20
30
40
50
60
70
80
90
TEMP. °C

TABLE XV.

Determination of the diffusion coefficient of Ethylene in Water.

Temp.	Time in Hours	Vol. of gas diffused S ml.	S at N.T.P. ml.	S/V ml/ml.	Mean conc. C of liq. ml/ml.	C_e ml/ml.	$D_{S.S.} \times 10^5$ $cm^2/sec.$
15°C	24	0.5	0.475	0.00795	0.00398	0.13502	1.34
25°C	24	0.65	0.595	0.00996	0.00498	0.10302	2.20
35°C	22	0.60	0.534	0.00894	0.00447	0.07903	2.80

TABLE XVI.

Determination of the diffusion coefficient of Carbon dioxide in Water.

Temp.	Time in Hours	Vol. of gas diffused S ml.	S at N.T.P. ml.	S/V ml/ml.	Mean conc. C of liq. ml/ml.	C_e ml/ml.	$D_{S.S.} \times 10^5$ $cm^2/sec.$
15°C	22	4.3	4.10	0.686	0.343	0.9847	1.73
25°C	24	4.55	4.10	0.0686	0.0343	0.7247	2.16
35°C	24	4.3	3.84	0.0642	0.0321	0.558	2.62
62°C	24	3.3	3.06	0.0512	0.0256	0.345	3.65
80°C	3.5	0.4	0.371	0.0062	0.0031	0.2119	4.35

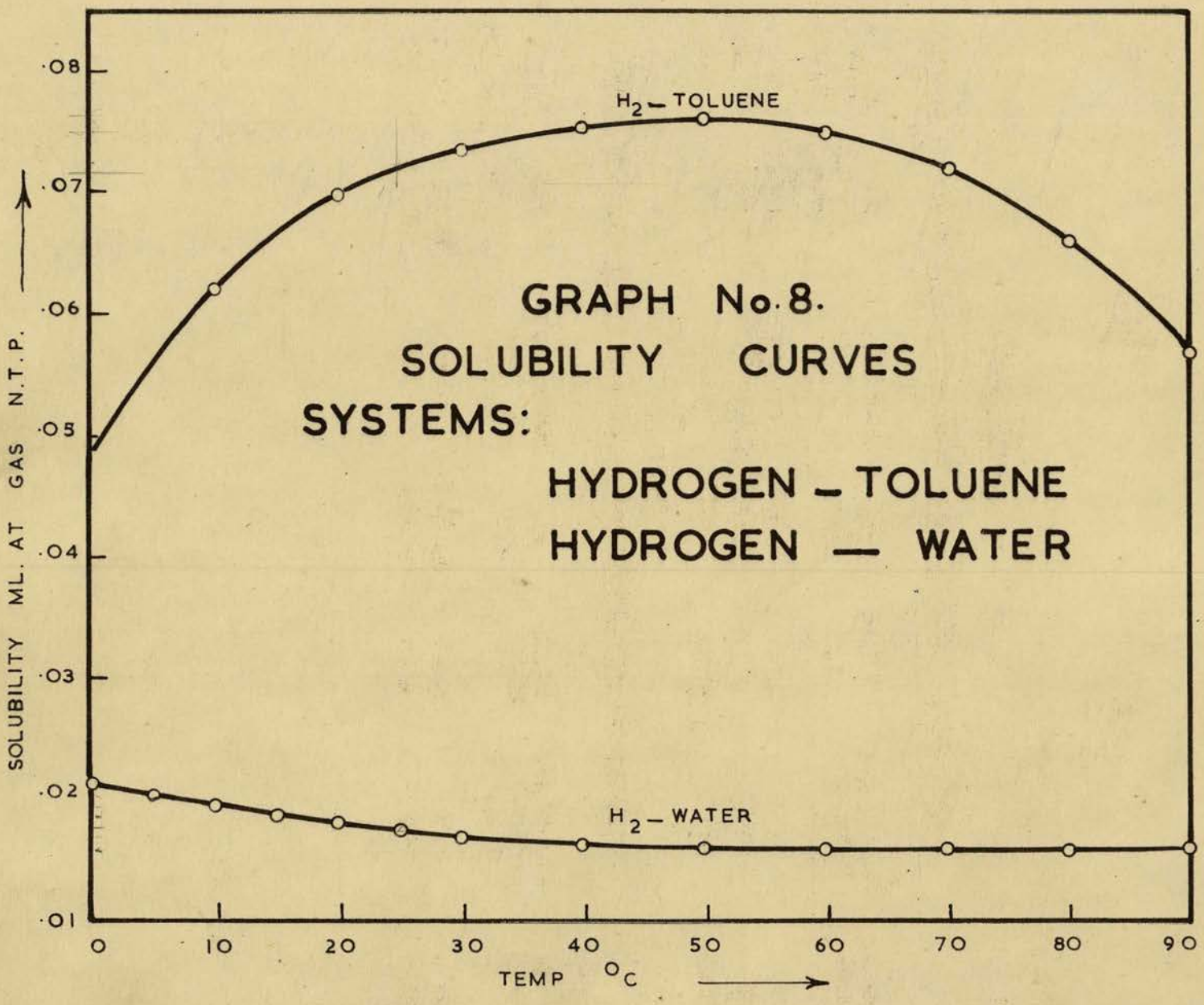

GRAPH No. 8.
SOLUBILITY CURVES
SYSTEMS:
HYDROGEN – TOLUENE
HYDROGEN — WATER
H2 – TOLUENE
H2 – WATER
SOLUBILITY ML. AT GAS N.T.P.
·08
·07
·06
·05
·04
·03
·02
·01
0
10
20
30
40
50
60
70
80
90
TEMP °C

TABLE XVII.

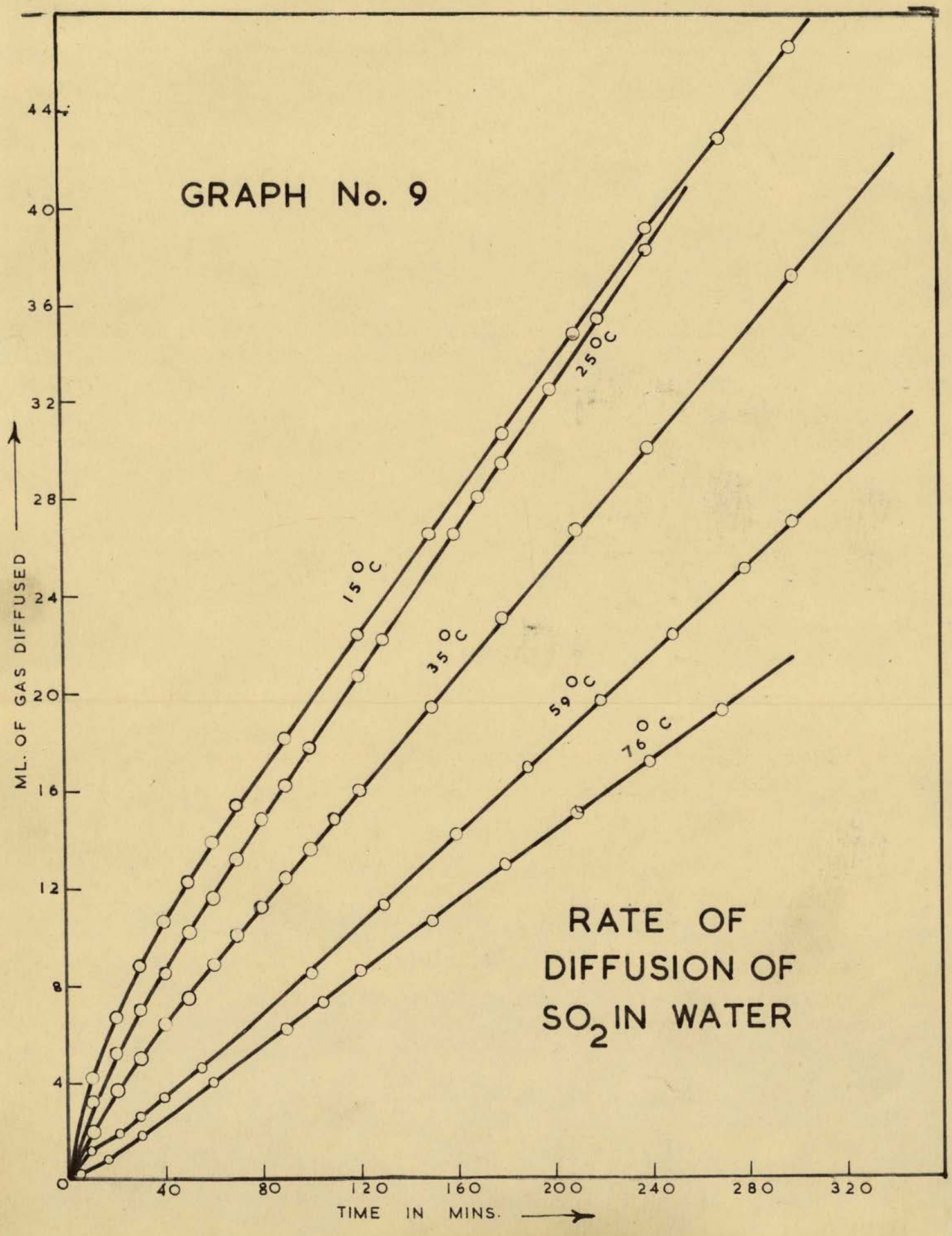
Determination of the diffusion coefficient of Hydrogen in Toluene.

Temp.	Time in Hours	Vol. of gas diffused S ml.	S at N.T.P. ml.	S/V ml/ml.	Mean conc. C of liq. ml/ml.	C_e ml/ml.	$D_{S.S.} \times 10^5$ $cm^2/sec.$
15°C	19	1.30	1.24	0.0207	0.0104	0.0567	10.5
25°C	20	1.40	1.272	0.0213	0.0107	0.0611	9.52
63°C	17.5	0.9	0.814	0.0136	0.0068	0.0672	6.32

TABLE XVIII.

Determination of the diffusion coefficient of Hydrogen in Water.

Temp.	Time in Hours	Vol. of gas diffused S ml.	S at N.T.P. ml.	S/V ml/ml.	Meanconc. C of liq. ml/ml.	C_e ml/ml.	$D_{S.S.} \times 10^5$ cm^2 Sec.
25°C	26	0.3	0.267	0.00446	0.00223	0.01533	6.10
35°C	22	0.3	0.267	0.00446	0.00223	0.01446	7.68


GRAPH No. 9
RATE OF DIFFUSION OF SO_2 IN WATER
ML. OF GAS DIFFUSED
TIME IN MINS.
0
4
8
12
16
20
24
28
32
36
40
44
40
80
120
160
200
240
280
320
15 O C
25 O C
35 O C
59 O C
76 O C

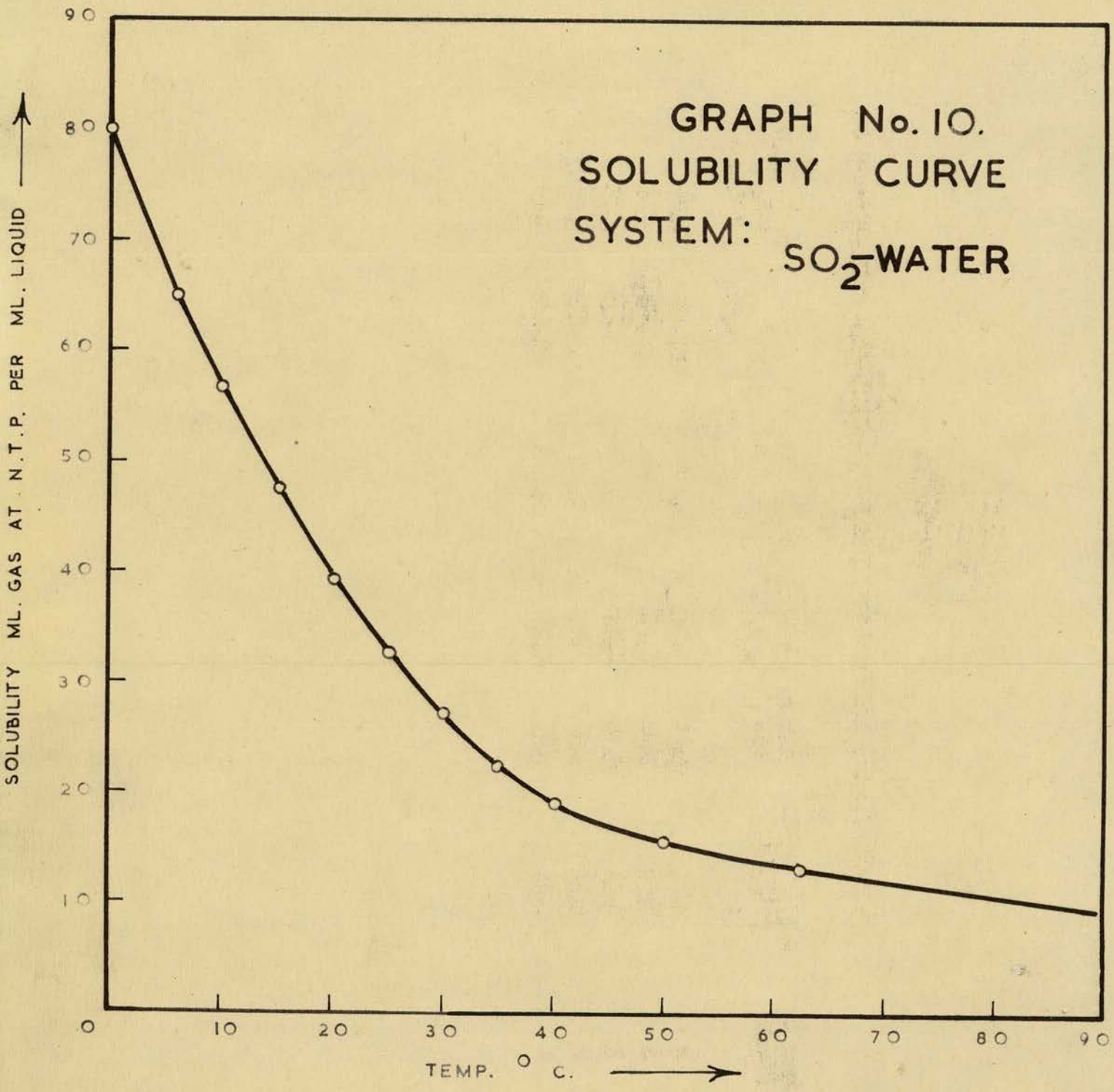

GRAPH No. 10.
SOLUBILITY CURVE
SYSTEM: SO_2-WATER
SOLUBILITY ML. GAS AT N.T.P. PER ML. LIQUID
TEMP. ° C.
0
10
20
30
40
50
60
70
80
90

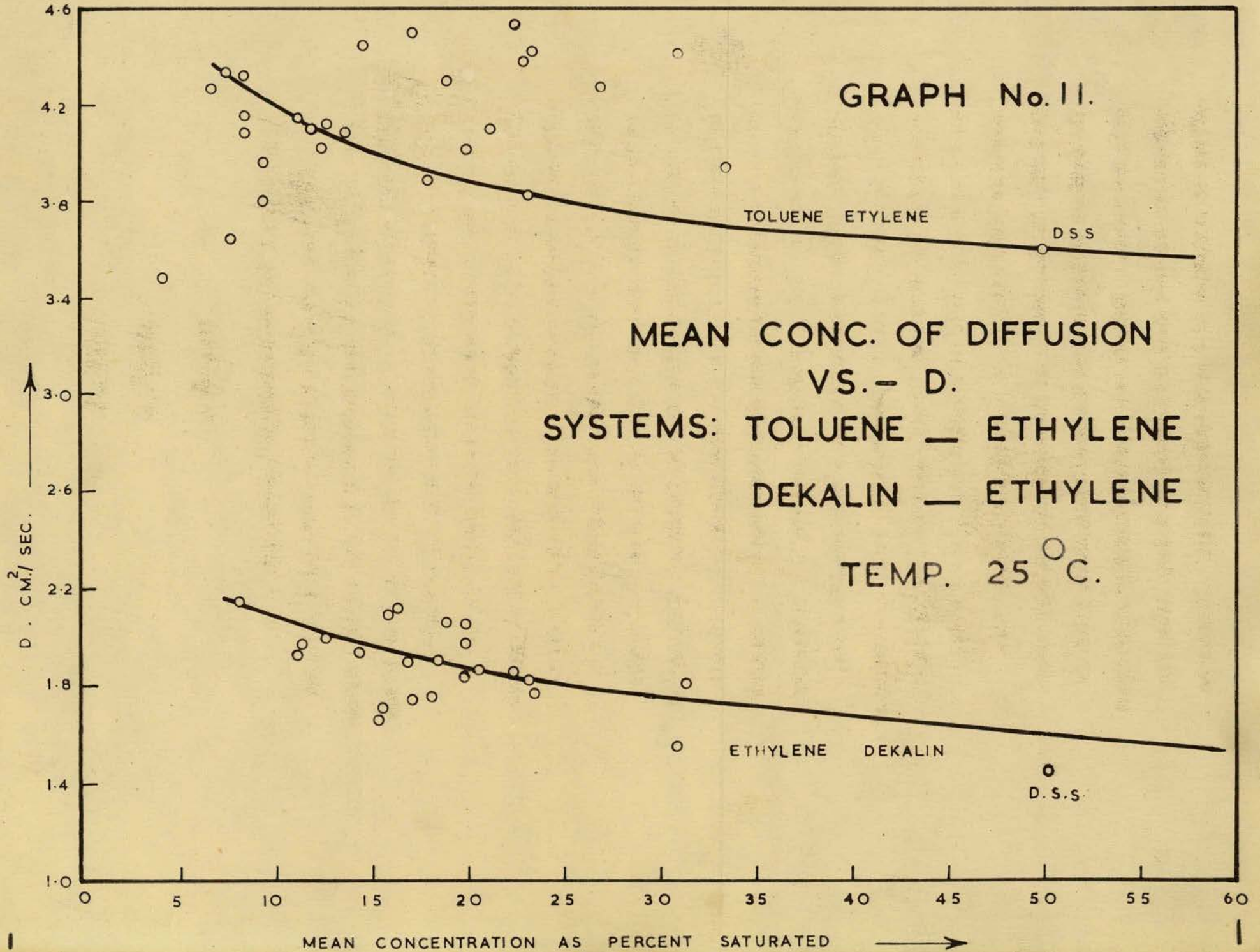
TABLE XIX.

Determination of the diffusion coefficient of Sulphur dioxide in Water.

Temp.	Time in Hours	Vol. of gas diffused S ml.	S at N.T.P. ml.	S/V ml/ml.	Mean conc. C of liq. ml/ml.	C_e ml/ml.	$D_{S.S_2}$ x 10^5 $cm^2/sec.$
15°C	1	8.3	7.95	0.132	0.066	47.214	1.58
25°C	1	8.775	7.81	0.131	0.0655	32.7245	2.18
35°C	1	7.05	6.34	0.106	0.053	22.437	2.58
59°C	1	5.45	4.91	0.082	0.041	13.809	3.25
76°C	1	4.25	3.88	0.065	0.0325	11.267	3.15

PART V

SECTION A


GRAPH No. 11.
MEAN CONC. OF DIFFUSION
VS.- D.
SYSTEMS: TOLUENE — ETHYLENE
DEKALIN — ETHYLENE
TEMP. 25 °C.
TOLUENE ETYLENE
D S S
ETHYLENE DEKALIN
D.S.S
D . CM.²/ SEC.
MEAN CONCENTRATION AS PERCENT SATURATED
4·6
4·2
3·8
3·4
3·0
2·6
2·2
1·8
1·4
1·0
0
5
10
15
20
25
30
35
40
45
50
55
60

PART V.

SECTION A.

Discussion

Comparison of the two methods for determining D.

As already noted, the diffusion coefficients of a few gases in liquids have been determined by two methods, measuring the gas dissolved in liquid and the gas as such in the upper compartment of the diffusion cell respectively. The values of D obtained by the former method on the assumption of a quasi-stationary state are plotted against the mean concentration at which diffusion takes place in Graph No. 11. It will be seen that the results show a scatter which is more pronounced in the case of diffusion of ethylene in toluene than that in dekalin. This may be assigned to the fact that the lower viscosity of toluene may have introduced greater error because of mass flow in certain runs. In spite of this, a smooth mean curve may be drawn showing the variation of D with concentration, which on extrapolation in both the cases point to a value of diffusivity for diffusion from a saturated solution to the pure liquid very close to that obtained by the latter method on the assumption of a stationary state. The variation in the results in themselves is not very great, the maximum deviation from the mean being about $\pm$ 12% in both the cases. This is not considered highly significant because of the fact that this deviation incorporates the effect of variation of D with concentration. It must be

admitted, however, that the method is incapable of giving results of very high precision because of the tendency of the gas to escape from solution when analysis is not carried out in situ. Another source of error by this method probably is the failure of the interference method for determining the concentration with the accuracy required, as a slight error in measuring concentration is magnified greatly in the resulting diffusion coefficient (23). It is found, however, that very consistent results may be obtained at high dilutions by this method if a sufficiently accurate analytical tool is available for the purpose. The method is not suitable for measuring diffusion coefficients of gases at concentrations more than half the saturation value.

The new technique for measuring diffusion coefficients of gases in liquids is considered to yield very satisfactory results and is found to be a most convenient method for the purpose. The method is capable of being extended to any gas-liquid system with a slight modification in its design and procedure. For instance, a very slightly soluble system may be tackled by employing a coarser sinter, a micro gas burrette, and a very sensitive Bourdon gauge. For highly soluble systems, a larger gas reservoir may be used with advantage. Since a very thin layer of liquid is used over the sinter surface, mass flow due to vibration or convection is negligible and coarser sinters giving higher diffusion rates should not cause any inconvenience. The A/L for such cells, however, must be determined by

employing a gas-liquid system of known D, as mass flow is likely to give higher values of cell constant if liquid-liquid system is employed for calibration. Experience has shown the last statement to be true, although time did not permit to verify the same experimentally.

In earlier experiments with this method, D has been calculated on the assumption of both stationary and quasi-stationary states. It is found that the values given by this method on the latter basis (table VIII) is too low compared to the values available in the literature while those on the former basis are comparable. This is to be expected on the basis of the fact that there is presumably no change in concentration of the liquid above the sinter while that below the sinter changes but little in the interval over which the coefficient is measured. This virtually corresponds to the existence of a stationary state. For this reason in later experiments D has been calculated on the basis of a stationary state only.

A great advantage of this technique lies in the fact that D can be measured over a desired concentration range which may be very narrow in some cases. Thus by plotting the amount of gas diffused against time, as has been done in the last part, D can be measured while the concentration of the liquid below the diaphragm is varying within a specified time interval. This, however, must be done after the steady conditions are established as shown by the straightening of the diffusion rate curve after an initial unsteady state period which is fairly long in certain cases, e.g., for the system sulphur dioxide - water

(Graph No. 9). In this way, D can be measured for an interval of even one minute in case of highly soluble gases while sufficient time, say twenty hours, must be allowed to measure D for scarcely soluble gases, if the sinter is not coarse enough and the gas measuring equipment is not sensitive enough to record the change accurately during shorter intervals.

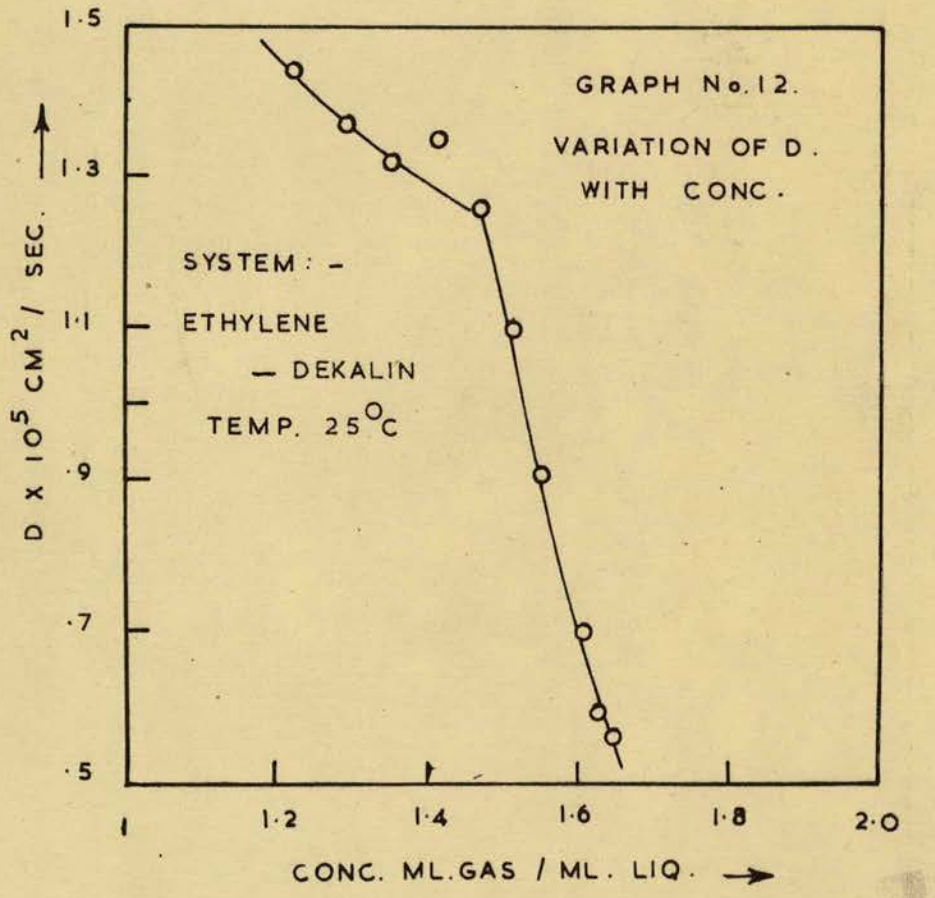
Some difficulty is encountered in working at higher temperatures by this method due to the fact that the gas and the liquid tend to expand as they attain the temperature of the experiment during the earlier stages of a run. This is avoided by letting the gas in after the liquid has attained the temperature of experiment and the surplus has been drained out from above the diaphragm. The gas, however, takes some time to attain the temperature of the thermostat and expands while doing so thus masking the actual amount of gas diffused during that interval. This may be seen clearly in Graph No. 9, where the initial rate of diffusion is actually lower than the steady state period at higher temperatures, some of the gas diffused being supplied by the expansion of the same. This cannot be avoided and the diffusion run should be reckoned after the gas has attained the temperature of the bath as shown by the attainment of a steady diffusion rate. At temperatures nearer the boiling point of the liquid, however, the gas has to be introduced at lower temperatures to avoid boiling during evacuation. As a result there is a thicker layer of liquid over the diaphragm after steady

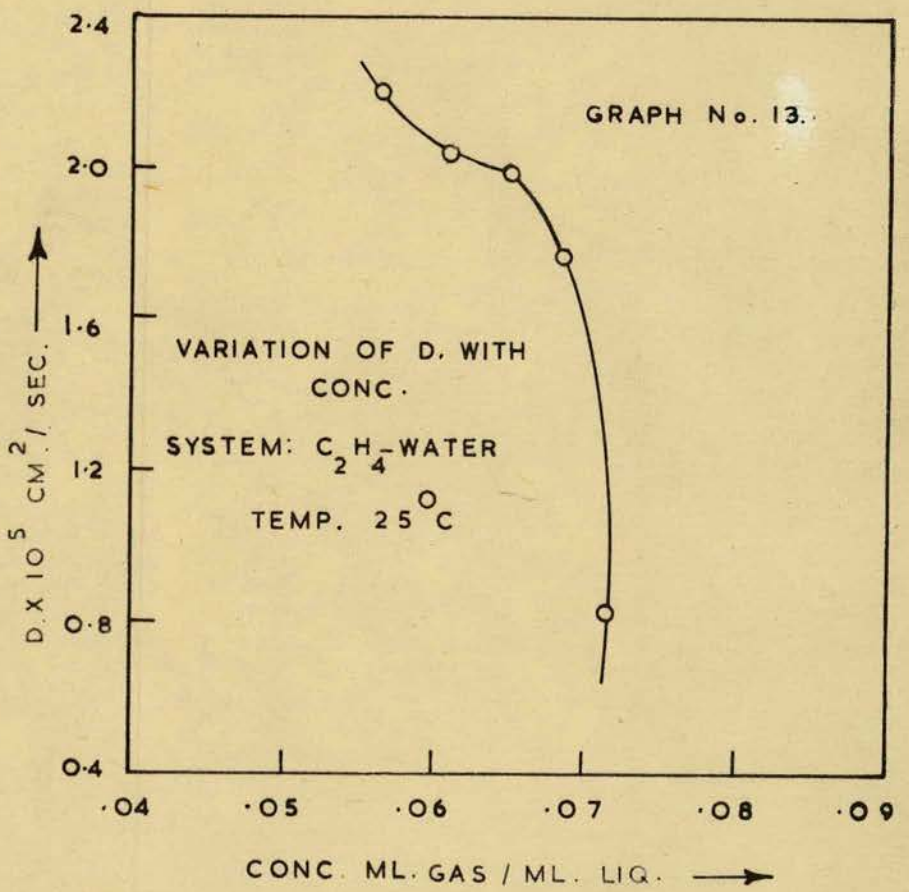
conditions are established, but the results do not indicate decisively that this layer is not completely saturated.

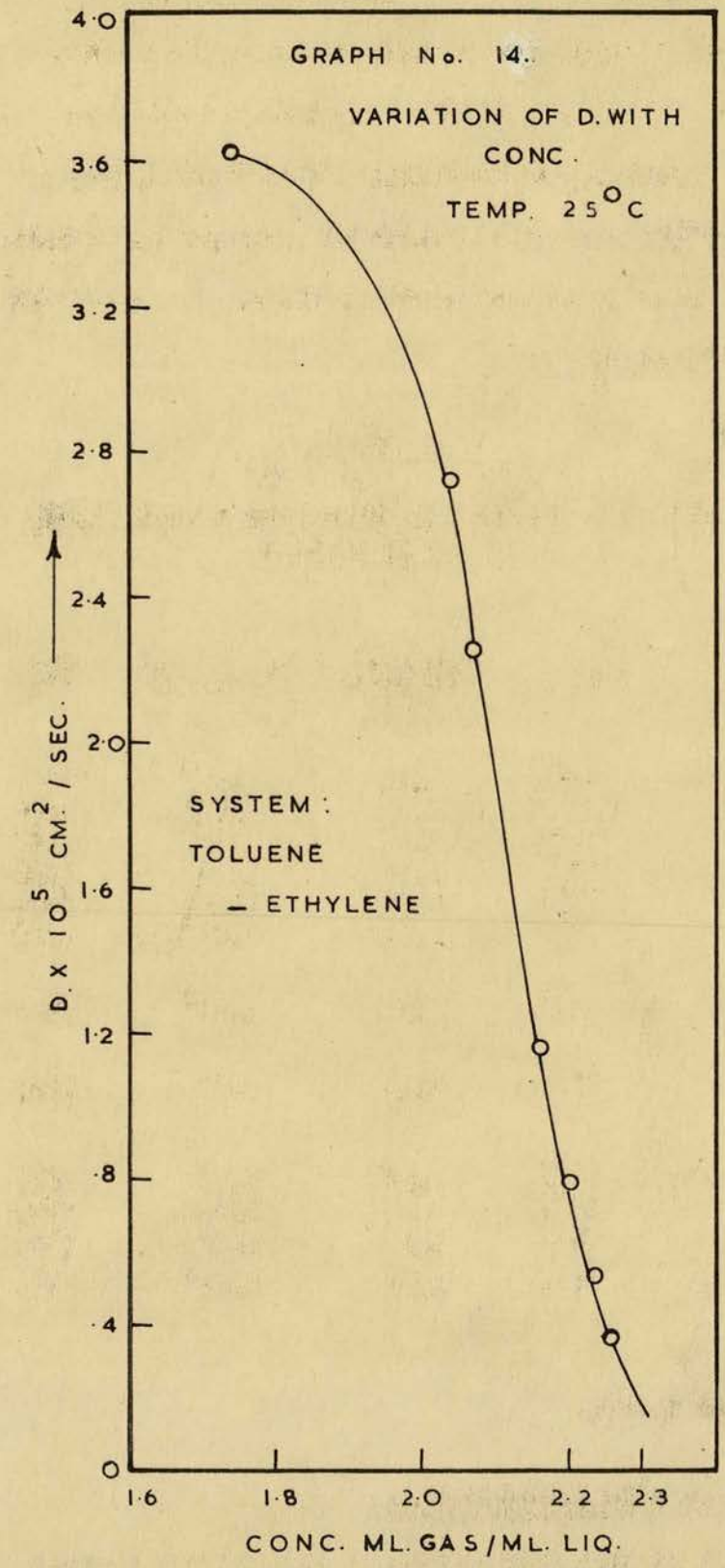
Another difficulty which is faced while measuring D by the new technique is the lack of data for solubility in many cases. In such cases, an estimate has to be made of solubility of the gas which may not be completely justified. For example, solubility values for ethylene in toluene in these experiments are estimated from those for ethylene in benzene and in xylene as shown in Graph No. 5. At higher temperatures, solubility values have to be obtained by extrapolation. These estimated values, in some cases, may not be very accurate, thus introducing an extra source of error in this technique in some cases. This can be avoided by measuring solubility of the system concerned in conjunction with diffusivity, whenever reliable data are not available.

It has already been pointed out that the method is incapable of yielding values of D for mean concentrations of less than half the saturation value, a fact which is not very critical for application of such values to rates of mass transfer. However, should it be necessary to obtain values of diffusivity in liquids in dilute solutions, recourse must be taken to the former method. This leads us to the inference that the two methods of measuring D are supplementary.

Diffusion coefficients of eight systems have been determined by the new technique which are reproducible within five per cent. Five different temperatures ranging from 15°C to 80°C for some systems are employed. In the


GRAPH No. 12.
VARIATION OF D. WITH CONC.
SYSTEM: -
ETHYLENE
— DEKALIN
TEMP. 25°C
D X 10⁵ CM² / SEC.
CONC. ML. GAS / ML. LIQ.
1·5
1·3
1·1
·9
·7
·5
1
1·2
1·4
1·6
1·8
2·0


GRAPH No. 13.
VARIATION OF D. WITH CONC.
SYSTEM: C₂H₄-WATER
TEMP. 25°C
D X 10⁵ CM² / SEC.
CONC. ML. GAS / ML. LIQ.
2·4
2·0
1·6
1·2
0·8
0·4
·04
·05
·06
·07
·08
·09


GRAPH No. 14.
VARIATION OF D. WITH CONC.
TEMP. 25°C
SYSTEM :
TOLUENE
– ETHYLENE
D. X 10^5 CM.^2 / SEC.
4·0
3·6
3·2
2·8
2·4
2·0
1·6
1·2
·8
·4
0
1·6
1·8
2·0
2·2
2·3
CONC. ML. GAS / ML. LIQ.

following table, the values of diffusivity obtained experimentally by the new technique are compared with those given in the literature. It will be seen that there is a good agreement between them. Some discrepancy is observed in the case of diffusion of hydrogen in toluene, but in all other cases estimated values are not very far from those observed.

TABLE XX.

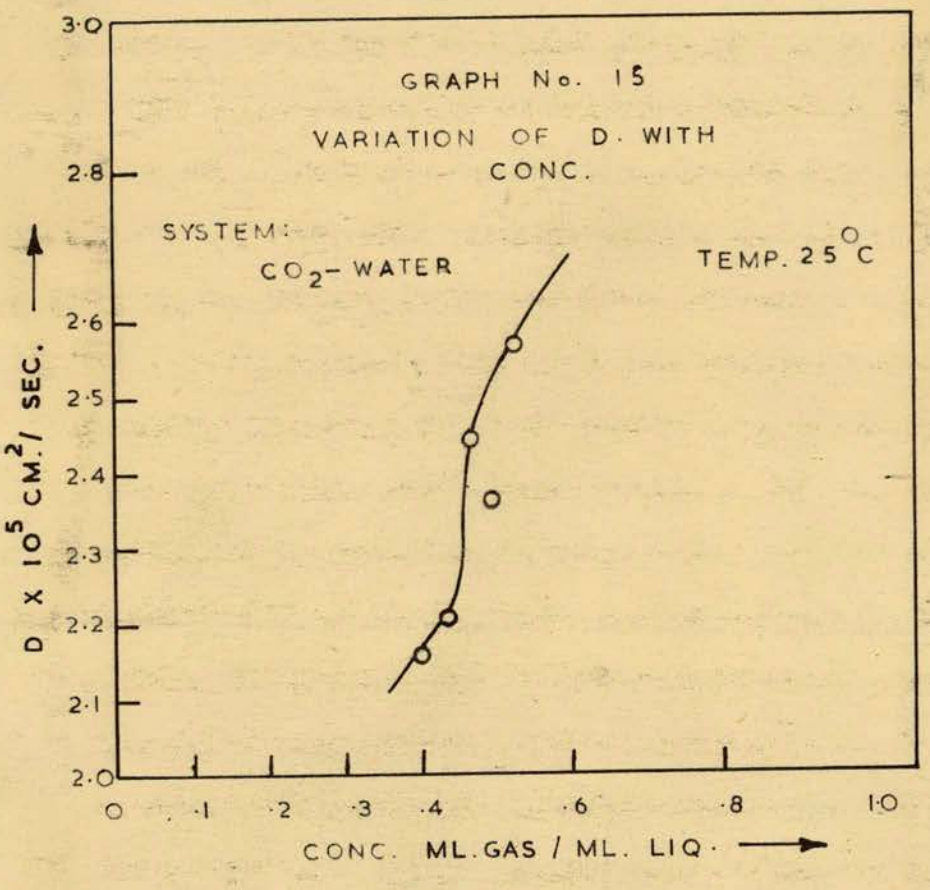
Comparison of experimentally determined D with values given in the literature.

System	Temp.	$D_{observed} \times 10^5$ $cm^2/sec.$	$D_{literature} \times 10^5$ $cm^2/sec.$	Ref.
Ethylene - Toluene	15°C	3.24	2.25*	(89)
	25°C	3.61	2.85*	(89)
	35°C	3.98	3.45*	(89)
	60°C	4.94	4.92*	(89)
	80°C	5.70	6.13*	(89)
Ethylene - Water	20°C	1.70	1.59*	(97)
Hydrogen - Toluene	25°C	9.52	5.60*	(89)
Hydrogen - Water	21°C	5.45	5.20	(98)
Carbondioxide - Water	10°C	1.45	1.46	(98)
	15°C	1.73	1.60	(98)
	20°C	1.96	1.77	(98)
Sulphurdioxide - Water	20°C	1.85	1.47*	(97)

* Estimated values.

Dependence of D on concentration.

It will be seen from Graphs 11, 12, 13 and 14 that generally the diffusion coefficient decreases with concentration as expected. Graph No. 11 obtained from

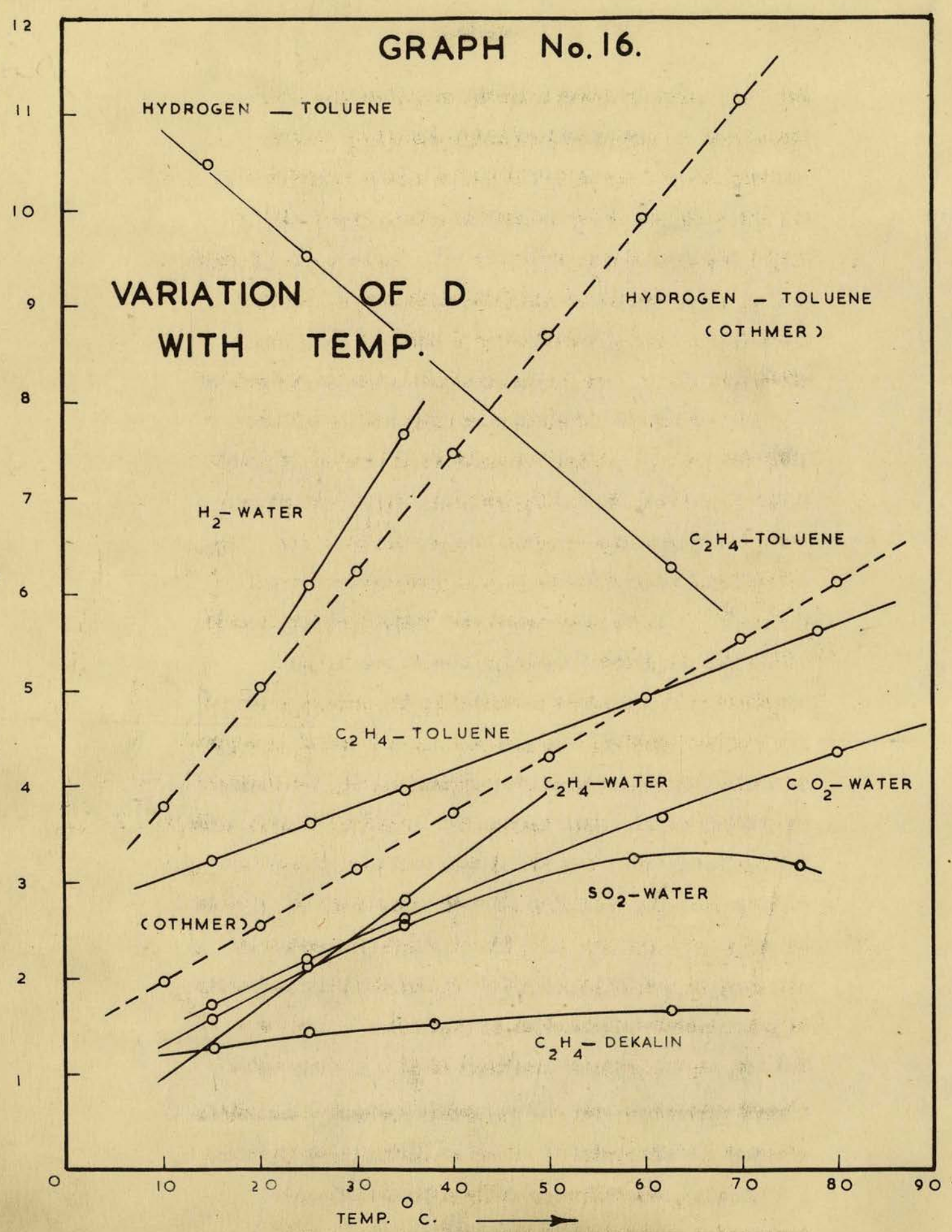

GRAPH No. 15
VARIATION OF D. WITH CONC.
SYSTEM:
CO_2 – WATER
TEMP. 25 °C
D X 10^5 CM.^{2}/ SEC.
3·0
2·8
2·6
2·5
2·4
2·3
2·2
2·1
2·0
0
·1
·2
·3
·4
·6
·8
1·0
CONC. ML. GAS / ML. LIQ.

the results by the older method shows a rapid decrease in diffusion coefficient with concentration in dilute solutions, but as the concentration increases, the diffusion coefficient decreases more slowly. This trend continues in Graphs 12, 13 and 14 obtained by the new method but there is a very rapid fall in D above the sixty per cent saturation value in each case. In fact, there is a break in the curves at that point for the diffusion of ethylene in water and in dekalin, but the change is not so pronounced in the case of diffusion in less viscous toluene. The last may be assigned to the fact that the point near which this break occurs has not been determined and it is quite probable that a determination of D between the first two points of Graph No. 14 may show a similar break. This rapid fall in D may be due to a higher ratio of reflection of the diffusing molecule from the surface of the liquid to actual penetration into the interstices after a certain concentration level.

It is interesting to note, however, that D actually increases with concentration in the case of diffusion of carbon dioxide in water (Graph No. 15). As this is the only system involving ions for which variation of D with concentration has been studied, this anomaly in behaviour may be assigned to that cause for it has been found that in general, rates of reactions involving ions are strongly affected by the total ionic concentration.

Variation of D with temperature.

Variation of diffusivity with temperature for the various systems is shown in Graph No. 16. It will be


GRAPH No. 16.
VARIATION OF D WITH TEMP.
HYDROGEN — TOLUENE
HYDROGEN — TOLUENE (OTHMER)
H2 — WATER
C2H4 — TOLUENE
C2H4 — TOLUENE
C2H4 — WATER
C O2 — WATER
SO2 — WATER
(OTHMER)
C2H4 — DEKALIN
D X 10^5 CM.^2/ SEC.
TEMP. °C.
0
10
20
30
40
50
60
70
80
90
1
2
3
4
5
6
7
8
9
10
11
12

seen that there is almost a linear variation of D with temperature in most cases, although there is a slight tendency for the curves to flatten at higher temperatures. The curve for the system sulphur dioxide - water shows a slight decrease in diffusivity at 76°C, although the probability of error because of employing extrapolated value of solubility or due to existence of a thick layer of liquid on the gas side of the diaphragm is not entirely improbable.

The curves for diffusivity in water and in toluene show much steeper gradient as expected on account of their lower viscosities and boiling points. The dotted curves are drawn from values computed from the nomogram for estimating diffusivities in liquids given by Othmer and Thaker[89]. It is to be noted that while the experimental values for the system ethylene - toluene are in good agreement with the values predicted by the nomogram, except for a higher gradient, the gradient for the system hydrogen - toluene is actually opposite in sign. This may be expected in view of the fact that whereas the solubility of most gases in liquids decrease with temperature that of hydrogen in toluene increases initially and then after about 50°C starts to decrease (Graph No. 8). Since methods of estimation are based on normal behaviour of systems only, the necessity of experimental determination in such cases is obvious. However, on the basis of constancy of $\frac{D}{T}\eta$, an increase in D with temperature even for the system hydrogen - toluene is expected and the system is worthy of further investigation.

Finally, the following table gives the percent temperature coefficient of diffusion for the various systems.

TABLE XXI.

System	Temperature Range	Per cent. temperature coefficient
Ethylene - Dekalin	15°C - 62.5°C	0.6
Ethylene - Toluene	15°C - 78°C	1.13
Ethylene - Water	15°C - 35°C	5.45
Hydrogen - Toluene	15°C - 63°C	-0.83
Hydrogen - Water	25°C - 35°C	2.59
Carbon dioxide - Water	15°C - 80°C	2.50
Sulphur dioxide - Water	15°C - 59°C	2.40

The value given by Arnold(86) is 3.0 at 20°C for diffusion in water which is in good agreement with the values for the last three systems. The high value for the diffusion of ethylene in water is a notable exception, which may be due to the fact that it is based on a temperature range of 20°C only, and since the solubility of ethylene in water is very low, the accuracy of determination is correspondingly lower.

Variation of D with viscosity of the medium.

A glance at Table VIII will show a decrease in the diffusivity of a substance with increasing viscosity of the liquid. Following table is computed to show how far the product $D\eta$ is constant.

TABLE XXII/

TABLE XXII.

System	Temp.	Viscosity η centipoises	D x 10^5 $cm^2/sec.$	Dη x 10^5
Ethylene - Dekalin	25°C	1.95	1.44	2.80
Ethylene - Water	25°C	0.87	2.20	1.92
Ethylene - Toluene	25°C	0.56	3.61	2.06
Hydrogen - Dekalin	25°C	1.95	3.30	6.44
Hydrogen - Water	25°C	0.87	6.10	5.31
Hydrogen - Toluene	25°C	0.56	9.52	5.33

It is seen that the product Dη is fairly constant for the solvents water and toluene but dekalin shows a higher value of the product in both the cases.

SECTION B.

Application of diffusivity in mass transfer.

Diffusivity and liquid film transfer coefficient.

It has been seen in Part II that k_L is expressed as a function of D in all the three models of absorption mechanism, the relationship being conveniently represented as:

$$k_L \propto D^x.$$

The following table is computed on the basis of experimentally determined values of k_L and D to show the relation between the two.

TABLE XXIII.

Determination of x.

System	Temp.	$Dx10^5 cm^2/sec.$	$k_L x10^3 cm/sec.$	Ref.	x
Hydrogen - Water	17°C	4.82	46.1	(35)	0.434
Ethylene - Water	17°C	1.50	27.8	(35)	
Hydrogen - Toluene	18°C	10.2	25.4	(93)	0.302
Ethylene - Toluene	16.2°C	3.28	18.0	(36)	
Carbon dioxide - Water	16°C	1.77	8.35	(36)	1.25
Ethylene - Toluene	16.2°C	3.28	18.0	(36)	

The first two values obtained on the basis of systems involving no chemical reactions are nearer 0.5 predicted by the relations of Higbie and of Danckwerts. The last value, which is obtained on the basis of one of the systems involving ions, is higher than unity and therefore it will be unreasonable to

draw any conclusion on that basis. However, it has been seen in Part II that the exponent of D found by other workers although quite near 0.5 is by no means constant and varies between 0.3 and 0.75. This suggests that the relation between D and k_L may not be as simple as postulated by the theories of Higbie and of Danckwerts and there may be some other factor involved, which may itself vary with the diffusivity of the system and possibly also with other variables to varying degree , so that k_L instead of varying with D with a fixed exponent, may vary with D with an exponent which itself varies within similar limits as found experimentally. It will be seen presently that δ in equation (57) is one such factor, which in itself may not be as represented by equation (57), but may lead to an insight into the mechanism of mass transfer.

Thickness of the surface film.

The following table gives the values of the thickness of surface film computed by substituting experimental values of D and k_L in equation (57).

TABLE XXIV/

TABLE XXIV.

Determination of δ.

System	Temperature	D x 10^5 cm^2/sec.	k_L x 10^3 cm/sec.	Reference	δ x 10^3 cm.
Sulphur dioxide - Water (jet)	16.8°C	1.70	7.23 - 11.57	(36)	2.33 - 1.47
Carbon dioxide - Water (jet)	16°C	1.77	5.70 - 8.35	(36)	3.11 - 2.12
Hydrogen - Water (bubbles)	17°C	4.82	46.1	(35)	1.05
Ethylene - Water (bubbles)	17°C	1.50	27.8	(35)	0.54
Ethylene - Toluene (bubbles)	18°C	3.35	2.93	(93)	1.11
Hydrogen - Toluene (bubbles)	18°C	10.2	25.4	(93)	4.01
Carbon dioxide - Water (bubbles)	17°C	1.82	27.8	(35)	0.655
Carbon dioxide - Water (film)	25°C	2.16	4.45	(12)	4.85
Ethylene - Toluene (jet)	16.2°C	3.28	17.35 - 18.7	(36)	1.89 - 1.75

These values of δ may be compared with the values of δ given by Brunner[99] for dissolution of solids in liquids.

TABLE XXV.

δ for dissolution of solids in liquids.

System	Temperature	$\delta \times 10^3$ cm.
Benzoic acid - Water	20°C	2 - 3
Magnesia - Benzoic acid	20°C	2.9
Magnesia - Acetic acid	20°C	2.8
Marble - Hydrochloric acid	20°C	3.2 - 3.6
Magnesium - Benzoic acid	20°C	2.2
Silver acetate - Water	20°C	3.1 - 3.9

It is interesting to note that the thickness of the stagnant layer is of the same order in the case of mass transfer between solids and liquids to mass transfer between gases and liquids. In some cases, where the thickness is lower, bubbles are involved and the lower thickness of the surface film may be assigned to turbulence in such systems. Hixson and Baum[100] have shown that δ is inversely proportional to the rate of stirring from 200 to 450 R.P.M. for dissolution of benzoic acid in caustic soda. However, it can be seen from table XXIV that although the film thickness is of the same order in all the cases of laminar flow, it varies with the properties of the medium and with flow conditions. For laminar flow along a flat plate, Levich[101] obtained the relation:

$$\delta = 3 x^{\frac{1}{2}} D^{\frac{1}{3}} \eta^{1/6} U^{-\frac{1}{2}} \quad \ldots\ldots\ldots (63)$$

where U is the characteristic velocity of the system and x is the distance from the edge of the plate.

Although the variation of δ with viscosity or flow conditions is quite understandable, it is difficult to see how it depends on the diffusivity of the system except for its effect on the properties of the medium. Assuming a normal distribution of the displacements of the diffusing molecules, as the diffusivity will increase, more molecules will be able to travel into a region where turbulence exists and the transport will be diffusion controlled to a lesser extent. Thus, although the physical thickness of the surface layer may not be affected by diffusivity of the system, the result will be as if it were, and that may account for Levich's observation.

It is often stated that the thickness of the stagnant layer, obtained by equation (57), which corresponds to a layer of about 50,000 molecules thick, is improbably high. Page and Townend[102] have shown that fluid motion persists to within a distance of 0.6×10^{-4} cm. from the wall of a pipe carrying a fluid in turbulent flow. However, this may not be inconsistent with the assumption that in a region near the interface of thickness δ' the liquid is in stream line flow where the concentration is a linear function of the distance y (measured normal to the surface) over the range $o \leqslant y \leqslant \delta'$ and the rate of mass transfer in that region is controlled by molecular diffusion. This region of thickness δ' may correspond in effect to a stagnant layer of effective thickness δ and that may account for the fact why the two film theory has been able to explain so many experimental observations. The inconsistency in the exponent of D in the relation $k_L \propto D^x$ may be due to the fact that this region where mass transfer is controlled by molecular

diffusion varies in thickness and depends on the properties of the medium, the flow conditions and probably also the temperature. This may be the reason why k_L does not always vary with $D^{0.5}$ as presented by the relations of Higbie and of Danckwerts which are yet to be confirmed experimentally.

The distance to which a diffusing molecule penetrates.

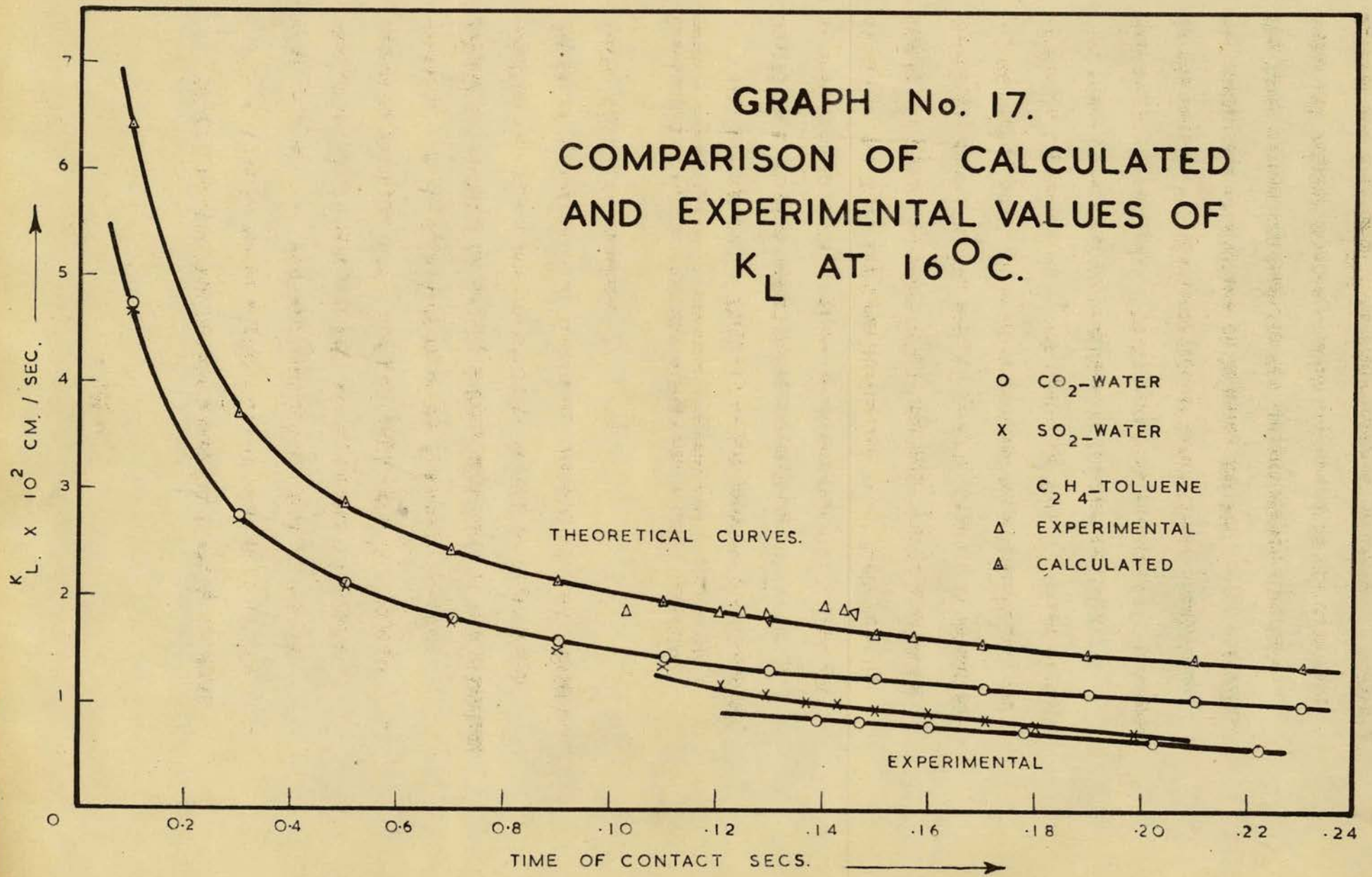
It will be interesting to know how far a diffusing molecule will penetrate on the average in a given time of contact and if this thickness is significantly different from the thickness of the region where mass transfer is mainly controlled by molecular diffusion. The following table is computed for determining $\bar{\Delta}$ from equation (44) by substituting experimentally determined D and known time of contact.

TABLE XXVI/

TABLE XXVI.

Determination of $\bar{\Delta}$.

System	Temperature	t. sec.	D x 10^5 cm^2/sec.	$\bar{\Delta}$ x 10^3 cm.	δ x 10^3 cm.
Sulphur dioxide - Water (jet)	16.8°C	.1213 - .1989	1.70	2.03 - 2.6	1.47 - 2.33
Carbon dioxide - Water (jet)	16°C	.139 - .222	1.77	2.22 - 2.8	2.12 - 3.11
Hydrogen - Water (bubbles)	17°C	.1	4.82	3.1	1.05
Ethylene - Water (bubbles)	17°C	.1	1.50	1.73	0.54
Ethylene - Toluene (bubbles)	18°C	.1	3.35	8.17	1.11
Hydrogen - Toluene (bubbles)	18°C	.1	10.2	14.2	4.01
Carbon dioxide - Water (bubbles)	17°C	.1	1.82	1.9	0.655
Carbon dioxide - Water (film)	25°C	.1	2.16	2.08	4.85
Ethylene - Toluene (jet)	16.2°C	.1037 - .1570	3.28	2.58 - 3.2	1.75 - 1.89


GRAPH No. 17.
COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES OF K_L AT 16°C.
K_L X 10^2 CM. / SEC.
TIME OF CONTACT SECS.
O CO_2-WATER
X SO_2-WATER
C_2H_4-TOLUENE
Δ EXPERIMENTAL
Δ CALCULATED
THEORETICAL CURVES.
EXPERIMENTAL
0
1
2
3
4
5
6
0·2
0·4
0·6
0·8
·10
·12
·14
·16
·18
·20
·22
·24

It will be seen that in most cases the distance to which a molecule penetrates in a given time of contact is of the same order as δ. The very high values obtained for the absorption of hydrogen and ethylene in toluene in bubble swarms is probably due to a higher estimate of the time of contact. If the distribution of the distances to which molecules penetrate is normal, a fair proportion of the molecules striking the liquid surface will not be able to penetrate a region of thickness δ and therefore transport will be diffusion controlled in that region.

Prediction of k_L for specific conditions of mass transfer.

As has been said in Part II, we can predict the values of liquid film transfer coefficients for various values of δ, t_e or S if D is known. Since it is not feasible to measure δ directly, and S has not been determined in conjunction with liquid film transfer coefficients for many systems, we shall confine ourselves to the prediction of k_L from known values of t_e and compare with the results obtained experimentally. In Graph No. 17, values of k_L are predicted from t_e = 0.01 to 0.24 for three systems and are compared with experimentally determined values (36). It is seen that the slope of the curve is the same in all the cases and at least in one case, viz., the absorption of ethylene in toluene, the two curves coincide. The lower values obtained for the systems carbon dioxide - water and sulphur dioxide - water may be due to the fact that k_L does not vary as $D^{0.5}$ in these cases as predicted by Higbie's relation. Another explanation for this discrepancy may be the

fact that each of these systems involve ionisation to varying degree while the solubility of sulphur dioxide in water is not very low so as to neglect the gas-film coefficient. The following table summarises the comparison for other systems where the variation of k_L with t_e has not been determined experimentally. Values calculated by Danckwerts' relation are also given on the basis of S = 8/sec. (12).

TABLE XXVII/

TABLE XXVII.

Comparison of theoretical and calculated values of k_L

System (bubbles)	Temperature	D x 10^5 cm^2/sec.	t_e sec.	S $sec.^{-1}$	k_L x 10^2 cm/sec.		
					Danckwerts	Higbie	Experimental
Hydrogen - Water	17°C	4.82	.1	8	1.96	2.47	4.61
Ethylene - Water	17°C	1.50	.1	8	1.09	1.38	2.78
Ethylene - Toluene	18°C	3.35	1	8	1.63	0.652	0.293
Hydrogen - Toluene	18°C	10.2	1	8	2.85	1.14	2.54
Carbon dioxide - Water	17°C	1.82	.1	8	1.46	1.52	2.78
Ethylene - Toluene	39.5°C	4.15	1	8	1.82	0.725	0.391
Ethylene - Toluene	64.2°C	5.10	1	8	2.02	0.803	0.722
Hydrogen - Toluene	39.5°C	8.35	1	8	2.58	1.03	3.50
Hydrogen - Toluene	64.2°C	6.20	1	8	2.22	0.887	4.20

It will be seen that whereas Higbie's equation gives a very good estimate of liquid film transfer coefficient with jets having known times of contact and in stream line flow, it usually gives low values in the case of transfer involving bubbles. Estimation of k_L from Higbie's relation should, therefore, be applied only in cases where absorption takes place in an effectively still liquid and time of contact is definitely known. The relation of Danckwerts, also gives lower values in most cases, but this is not an adequate test for the relation at all as same value of S is used throughout. It is essential to estimate S accurately in systems for which k_L is being measured in order to test the adequacy of the relation and predicting values of k_L from the same.

CONCLUSIONS.

The following conclusions may be drawn from the results obtained by the two methods of determining diffusivity and their application to mass transfer between gases and liquids.

1) The diaphragm cell method may be conveniently adapted to measure diffusivity of gases in liquids. For measuring diffusivity in dilute solutions, the gas must be used in solution in one of the compartments and diffusivity measured on the basis of existence of a quasi-stationary state. This procedure is incapable of giving very accurate results if methods of analysis in situ or a very accurate method of analysis outside the system is not available. The method is unsuitable for very slightly soluble gases and for measuring variation of diffusivity with concentration.

2) The new technique for measuring diffusivity of gases in liquids using the gas as such in the upper compartment of the diffusion cell is capable of giving very accurate results for diffusivity in solutions at concentration more than half the saturation value. The diffusion coefficient obtained by this method is the one which should be applied in calculations involving mass transfer from pure gases to pure liquids, as this coefficient is measured

under similar conditions. It has been found that a stationary state exists in the diaphragm and the results obtained on this basis are comparable with those in the literature. The technique may also be applied to systems having very low solubility by employing a coarser sinter and a micro-burrette. Variation of diffusivity with concentration as well as with temperature may be measured conveniently by this method. At temperatures near the boiling point of the liquid, however, a thick layer of the liquid has to be left on the sinter surface which may become a source of error in certain cases because of not being completely saturated.

3) Use of extrapolated values of solubility may sometimes be a source of error in determining diffusivity by the new technique and therefore, in the absence of reliable data on solubility, diffusivity should be measured in conjunction with solubility.

4) Methods of estimation of diffusivity should be used with caution for determining variation of D with temperature especially if the variation of solubility with temperature shows some abnormality. The same applies to determination of variation with concentration if the system involves ionisation.

5) The diffusivity of gases in liquids usually decreases with concentration, the decrease being very rapid after a mean concentration of diffusion of about sixty per cent

the saturation value. The diffusion of carbon dioxide in water is a notable exception.

6) The diffusivity of gases in liquids usually increases with temperature, the plot of D vs. temperature being approximately linear in most cases. The diffusivity of hydrogen in toluene and of sulphur dioxide in water above $60^{\circ}C$, however, show a decrease and need further investigation. The slope of the curve D vs. temperature generally decreases with the viscosity of the medium.

7) The diffusivity of gases in liquids is an inverse function of the viscosity of the medium.

8) Experimental data suggest that liquid film transfer coefficient may not vary with diffusivity with a fixed exponent as required by the relations of Higbie and of Danckwerts but with an exponent varying within narrow limits.

9) In spite of statements of the physical improbability of existence of a stagnant layer of liquid of macromolecular dimensions at the interface, it is quite possible that the rate of mass transfer is controlled by molecular diffusion in a region at the interface the thickness of which is a function of the properties of the medium and of flow conditions. This may also explain why k_L does not vary with D with a fixed exponent.

10) That mass transfer is controlled by molecular diffusion in a region near the interface is also suggested by the average

distance travelled by a diffusing molecule in a given time of contact.

11) In spite of its limitations, Higbie's equation gives a fair estimate of liquid film transfer coefficients for mass transfer into effectively still liquids which do not involve chemical reaction, but gives low values generally in cases involving bubbles. The equation of Danckwerts cannot be examined adequately due to lack of sufficiently precise data for the rate of surface renewal in conjunction with liquid film transfer coefficients.

Suggestions for further work.

1) Determination of the solubilities of the systems for which estimated values are used to confirm the results.

2) Determination of diffusivity in conjunction with solubility at still higher temperatures.

3) Employment of coarser sinters and microburrettes to prove the suitability of the new technique for determining diffusivity of slightly soluble gases with higher accuracy.

4) Further investigation of the diffusivity of hydrogen in toluene and of sulphur dioxide in water at high temperatures.

5) Further investigation of the variation of diffusivity with concentration of carbon dioxide in water and of ethylene in toluene.

6) Investigation into the possibility of employing diffusion channels of known dimensions, say by employing a plastic disc with holes of known dimensions by dissolving metallic wires previously impregnated into it.

7) Correlation of further data on k_L and D for non-reacting systems to confirm the variation of the exponent of D.

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NOMENCLATURE.

A = effective cross-sectional area
A_1, A_2 = constants
B = constant
C = volumetric concentration of diffusing gas
c = concentration
D = diffusion coefficient
E = eddy diffusivity
H = Henry's Law constant
K = constant
k_L, k_G = film coefficients
L = latent heat of evaporation
L, l, $\neq L_\varphi$ = effective length, characteristic length
M = molecular weight
p = partial pressure (p.25, osmotic pressure)
Q = feed rate
R = distance
r = radius
S = volume of gas diffusing
S = rate of surface renewal, sum of cube roots (as defined)
T = temperature
t = time
u = velocity
V, v = volume
x, y, z = coordinates
Z = viscosity in centipoises
x = axial distance
η, μ = viscosity
λ = distance
δ = equivalent film thickness

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King's Buildings,
The University,
Edinburgh.

Narain P. Agarwalla.
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